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THE SPECIFIC HEATS OF THE METALS.

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A REVIEW of the work which has been done in determinations of the specific heats of the metals by those whose results have been generally received as creditable, renders evident the difficulty of obtaining a satisfactory series of results. A classification of the sources of error in such work leads us to a consideration of the following:—

I.

The Purity of the Metals Used.

Obviously no method, however satisfactory in principle or carefully undertaken, can give satisfactory results if such results are condemned from the beginning because of the nature of the metal used. Yet the majority of published results are obtained by use of somewhat impure materials. In some cases this was due to the opinion that a slight degree of impurity might be considered negligible; but in the greater number of cases it was due to the difficulty of obtaining metals as nearly absolutely pure as could be prepared. There is, therefore, much uncertainty as to the meaning of the terms "pure," "nearly pure," etc., as applied to metals used, as few investigators have presented chemical analyses. The development of chemical methods for the purification of metals has, however, rendered it possible at the present time for investi-

gators to secure materials much more nearly pure than those formerly available, and, in this respect at least, recent work should carry more weight than that of former investigators. In addition to this uncertainty as to the purity of the metals used, attention should be called to the condition and previous treatment of the metals. We note determinations made upon metals powdered, in small fragments, crystalline, cast into small or large masses, drawn into rods or wires, or rolled into sheets. It is well known that molecular structural changes produced by mechanical operations produce a very perceptible change in the specific heat of a metal. Results obtained from metals which have been subjected to such diverse treatment are, therefore, not properly comparable. It is also probable that determinations made by use of powdered metal are somewhat higher than they should be, owing to the effect of the heated air carried into the calorimeter cup among the small fragments.

II.

The Determination of Temperatures.

In this we have a source of error, common to all calorimetric methods, which is undoubtedly the cause of many of the discrepancies observed in the results obtained. All the difficulties involved in the exact use of mercurial thermometers are concerned in this. It would appear that undue reliance has been placed upon the degree of accuracy obtainable by the correction of the readings of the thermometers which have generally been used. This holds true especially in the case of thermometers used for determining temperatures somewhat above or below room temperature when a correction for stem exposure has been applied. The methods employed for standardizing thermometers have also often given untrustworthy results, thus introducing constant errors.

III.

The Methods Employed.

Of the many calorimetric methods that have been devised, those most worthy of consideration are based upon the heat equivalent

of fusion of ice, the heat equivalent of vaporization of water, and the change in temperature produced in a liquid by the immersion of a body of different temperature.

The first of these methods, commonly known as the method of melting ice, has been best applied by use of the well-known form of Bunsen's ice calorimeter. It is unfortunate that this calorimeter, which appears theoretically so satisfactory, is found to be deficient in accuracy in operation. The sources of error, exclusive of errors of thermometry common to all methods, are chiefly those arising from the dependence of the results upon the calibration of the instrument by use of previous determinations of the specific gravity of ice, and those arising from uncertain "rate" of motion of the mercury in the capillary tube. As to the former, it is obvious that the differing results obtained by different investigators, varying from 0.905 to 0.950, suggest doubt as to the accuracy of results based upon a quantity the value of which appears so uncertain. As to the latter, the effect of slight impurities in the snow or ice surrounding the calorimeter is to cause such a constant deposition of ice on the ice cylinder as to cause the mercury thread to move many scale divisions in a minute. This motion, even under favorable conditions, is not exactly proportional to the time, and often occurs in a very irregular manner, thus rendering uncertain the confidence which may be placed in the indications of the mercury thread when corrected for "rate" of motion. This calorimeter is also subject to error in failure to exclude absorbed air from the instrument when first filled. This can be done if the operation is conducted with great care, but it is doubtful whether operators have usually been successful in this respect. The fact that the above sources of error have rendered the results obtained by use of this calorimeter somewhat doubtful is rendered evident by a review of the best results obtained. We note that the results obtained by different investigators are not concordant, that they do not agree well with results obtained by other methods, and that even the results obtained by the same person using the same material on different occasions are not concordant. Attention will be called to this later. At present it may be sufficient to cite the results obtained by Bunsen for calcium, — 0.1722 and 0.1688, —

showing a difference of 2 per cent in the values as determined by one presumably thoroughly conversant with the best methods of procedure with this calorimeter. It should, however, be borne in mind that this method was designed especially for the determination of the specific heats of the rare elements, of which but a small quantity may be obtained in a pure state, and for this purpose it has been most frequently applied.

Upon the heat equivalent of vaporization of water has been based the method of condensation as applied in the gravimetric calorimeter devised by Dr. J. Joly. The principle applied is simple. If a given mass of a substance at known temperature be plunged into steam, it experiences a rise in temperature and absorbs a number of calories of heat from the steam which is condensed upon its surface. The heat equivalent of vaporization of water at the given temperature being known, we have to determine the temperatures and the weights of the given body, before and after the condensation of steam upon its surface, to obtain the necessary data. The most important conditions of operation are thus: Sudden replacement of the air surrounding the substance by the vapor to be condensed; perfect mechanical conditions permitting the evaluation of the weight condensed while the substance is still surrounded by the vapor. In practice, however, several corrections must be applied. The weight of steam condensed upon the bucket which holds the given substance must be determined from preliminary experiments for the given temperature range and subtracted from the total weight of steam deposited. Correction to the weight of the body when immersed in steam must be made, owing to the different densities of steam and air. Exclusive of errors of thermometry this method is, therefore, subject to the following sources of error: Errors arising from the application of the correction factors; loss of water condensed upon the bucket which may drop from time to time; variations produced by deposition of water upon the suspension wire at the point at which it enters the steam chamber; a constant dependence upon the accuracy of the values previously determined for the heat equivalent of vaporization of water at the given temperature. It is evident, therefore, that although results obtained by

this method may agree quite closely among themselves, there may be constant errors in a series of observations which may render the results less worthy of confidence than the method might at first promise.

The third method, commonly known as the method of mixtures, was first successfully applied by Victor Regnault, and, as described in his classic researches, it deserves especial attention. This method, as applied by Regnault and his followers, together with its modifications, has yielded the best results thus far obtained in all cases in which a considerable mass of pure metal might be obtained. This fact is readily attested by a comparison of the greater uniformity of the results obtained by different observers employing this method at various times as compared with results obtained by other methods. The facilities available for his work, and the extraordinary ability in overcoming experimental difficulties which he possessed, render Regnault's work admirable in many respects. Without entering into details as to the familiar apparatus used and its operation, it is perhaps sufficient to say that probably the greatest source of error in the application of this method is found in the calculation of the radiation correction. This correction factor has been applied by Regnault's followers in practically the same manner as he applied it. For the purpose of avoiding the necessity for the determination of this factor, and consequently any errors which may arise from it, Prof. M. N. Hesehus[1] has suggested that the calorimeter cup be introduced into the bulb of an air thermometer and maintained at a constant temperature by the introduction of a sufficient amount of cold water, of known temperature, immediately after the introduction of the heated solid. By this means the correction for radiation and that due to the "water equivalent" of the calorimeter cup are avoided. The heat received by the cold water being equal to that given out by the heated body, the following simple equations may be used: —

$$MS(T-\theta) = ms(\theta - t),$$

[1] Journal de la Société Physico-chemique Russe, Nov. 1887; Journal de Physique, tom. vii., p. 489, 1888.

in which

M = mass of substance, the specific heat of which is to be determined.
m = mass of cold water introduced into the calorimeter cup.
T = temperature of the heated body.
θ = initial temperature of the calorimeter cup.
t = temperature of cold water introduced into the calorimeter cup.
s = mean specific heat of water at temperature used.
S = specific heat sought.

From this equation we have

$$S = \frac{ms(\theta - t)}{M(T - \theta)},$$

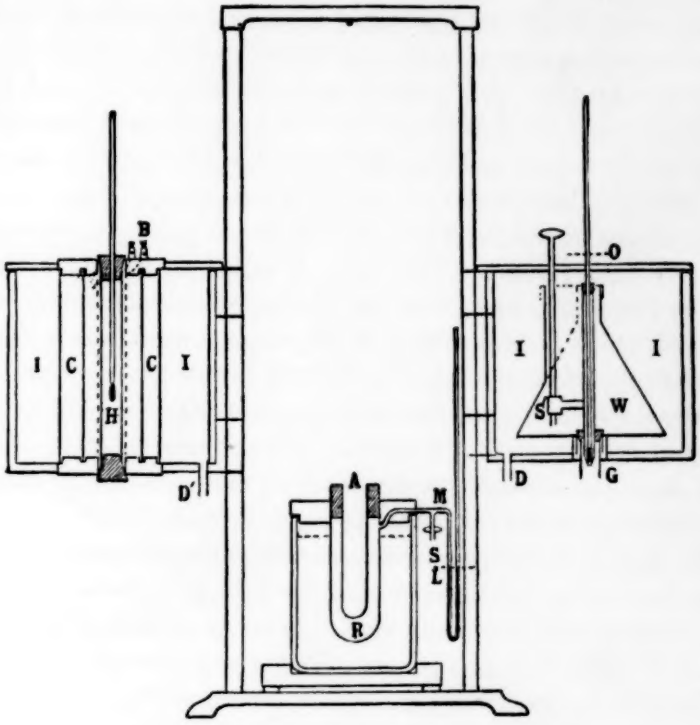
the working equation used.

The results obtained by this method, however, as submitted by Professor Hesehus, do not appear tc be as accurate as those obtained by the method of mixtures as practiced by Regnault. The ten determinations given of the specific heat of brass varied from 0.0821 to 0.0969, or, omitting the result, 0.0821, which was apparently erroneous, nine determinations varied from 0.0908 to 0.0969, the probable error of the mean of the whole being much higher than is usual in the case of a similar series of results obtained by Regnault's method. As the method suggested by Professor Hesehus appears to be a desirable one, I have endeavored to perfect a calorimeter by means of which it might be applied with greater accuracy. The form of apparatus which I have devised has proved very satisfactory, after repeated trials, as is shown by the results submitted. It consists essentially of the following parts: —

A glass jar which supports, by a wooden cover, the bulb R of a glass air thermometer, the manometric tube M of which, in the form of a capillary U-tube, is supported in a vertical position. The manometric tube is supplied with a stopcock S. The glass jar is kept nearly full of water for the purpose of maintaining the thermometer bulb constantly at room temperature and preventing any sudden variation of temperature due to air currents. For the purpose of increasing the sensitiveness of the thermometer, the

liquid selected was one of low density, and kerosene, of specific gravity approximately 0.8, was taken. The air thermometer thus constructed proved very sensitive, and a change in the temperature of the calorimeter cup of 0°.01 C. was clearly shown by an elevation of the manometric column.

The calorimeter cup *A* is made in the form of a tube of silver, 0.1 millimeter in thickness, of the general form of a test tube,



cemented to a rubber stopper which may be inserted air-tight into the thermometer bulb. This device was first used, but the calorimeter as now made has an air-tight connection at this part, similar to that used in the calorimeter for the method of cooling as usually applied. All errors due to leakage of air at stopper, etc., which might arise at this point, are thus avoided. Silver was selected as the material used for the cup on account of its high conductivity for heat, which causes the temperature of the cup to quickly

become that of its contents. The lower half of the outer surface of the tube is coated with a thin layer of lampblack mixed with turpentine and shellac for the purpose of increasing its radiating power.

The water cooler and dropper is supported upon a vertical rod in such a manner that it may be quickly turned about the rod as an axis, and may deliver water directly to the calorimeter cup. The cooler consists of a copper receiver, covered with heavy felt, within which the water receiver W is placed. A drainage tube D, provided with a rubber tube connection, conducts away the water from the melting ice I with which the receiver is filled. The water receiver W is made in the form of a cone of tin-plated copper. This form has been found most satisfactory for maintaining the water at constant temperature, as the ice, resting upon the sides of the receiver, cannot melt away from them, leaving an intervening air space. The water dropper consists of a siphon, within the longer arm of which a thermometer is introduced, the bulb of which is held very near the small orifice from which the water drops when the stopcock S' is opened. Thus no barrier is interposed at any time between the thermometer bulb and the point of delivery of the cold water. The zero point of the scale is just above the cover of the ice receiver, the stem being immersed in cold water nearly up to that point.

An electric heater is supported upon a second vertical rod, and may be turned about the rod as an axis until the heater H is directly over the calorimeter cup, allowing the heated body to be transferred directly to the cup. The heater, which is somewhat similar in form to that devised by Prof. Henry Crew,[1] consists of a copper tube H, about which is wound a heating coil of iron wire, insulated from the tube by narrow strips of asbestos paper. This is inclosed within a larger tube, and all is inserted within an ice receiver I, the space C being packed with cotton to prevent convection currents in the inclosed air. Water from the melting ice of the ice receiver escapes from the drainage tube D' by means of a rubber tube connection. The temperature of the outer wall remaining constantly that of the melting ice, the fall of tempera-

[1] Philosophical Magazine (5), 33, 1892.

ture remains constant between the inner and outer walls as long as heat is uniformly supplied to the inner chamber. This is readily maintained by a constant electric current supplied to the heating coil, through the binding screws *B*, from a storage battery of sufficient capacity having a variable resistance in its circuit. The battery which has been used maintained a normal electromotive force of 100 volts. The temperature of the heater is readily maintained constant within 0°.1 C. for any time required, at any temperature desired for the conditions of the work in hand, from 0.2 to 0.6 ampere of current being required according to the temperature desired. The thermometer for the determination of the temperature of the heated body is supported by a cork inserted in the top of the tube *H*. The bottom of the tube is provided with a sliding cover which remains closed while the body is heating, and automatically opens as the heater is turned around into position to deliver the heated body to the calorimeter cup.

The method of making a determination of the specific heat of a metal by means of this calorimeter is as follows: —

The metal may be suspended in the heater in small fragments, contained in a basket of fine wire gauze of known specific heat, as employed by Regnault; or, if in the form of sheet metal or fine wire, may be suspended in contact with the thermometer bulb by a thread of known weight. In the case of metals of low melting-points I have cast thin cylinders, slightly smaller in diameter than the calorimeter cup, which were so suspended in the heater that the bulb of the thermometer was within the cylinder while heating. The metal is then maintained at the desired temperature from one-half to three-quarters of an hour, according to its conductivity. The silver tube, which forms the calorimeter cup, is then withdrawn from the bulb of the air thermometer, pure water at room temperature is introduced in sufficient quantity to cover the metal used, and the whole is weighed. The cup is then placed in position in the bulb of the air thermometer, the stopcock *S* being opened while the rubber stopper is pressed firmly into place to insure an air-tight joint. Any "crawling" of the rubber stopper is easily detected by closing the stopcock *S*, and observing whether the manometric column remains stationary. A few

moments are allowed for this observation in each experiment. Any variation in the temperature of the cup is also readily detected in this observation. In each observation the manometric column has been found to remain stationary after a very short time. The initial temperature of the calorimeter cup, which remains at room temperature, is then taken by means of a thermometer suspended within the cup, having its bulb in contact with the side of the cup but not touching the water. This is found to remain practically constant throughout a series of observations, agreeing with the temperature of the water in the jar. Water is allowed to drop from the water dropper and its thermometer read as soon as its temperature becomes constant. This occurs after a few drops have fallen. The manometric column is then brought to the same level L in each arm of the U-tube by opening the stopcock S. A strip of white cardboard attached to the U-tube, with a horizontal ink-line at the back of the level surface of the manometric liquid, renders the position of the liquid column plainly visible. The stopcock is then closed, the heater turned around into position, and the heated metal quickly introduced into the cup. The heater is then turned back and the water dropper quickly turned into position, and water is allowed to drop into the cup, at first rapidly, then more slowly, until the manometric column remains at its original position, indicating that the initial temperature of the cup has been maintained. For several moments the manometric column is then observed, in order to make sure that the heated body has acquired the exact temperature of the cup. In the case of a body of low conductivity the cold water is more slowly introduced, as the heat from the body is more slowly transmitted to the water. The specific heats of substances of poor conductivity may thus be obtained with great exactness; the mixture being practically at room temperature, radiation loss is inappreciable during the time spent in observing the manometric column, and in adding water just sufficient in amount to maintain the initial temperature of the cup.

A little practice in the manipulation of the calorimeter enables the operator to keep the cup practically at its initial temperature throughout each determination, thus obviating the use of radiation

correction and "water equivalent" of the cup. The falling of the cold water from the water dropper into the tube-shaped cup also serves to agitate the water in the cup, and keeps its temperature uniform without the use of a stirrer. The cup and its contents are then removed from the bulb of the air thermometer and weighed. The weight thus obtained, minus the initial weight of the cup, water contained, and weight of metal used, gives the weight of cold water added. The loss in weight due to the evaporation of the water in the cup, during the time required for the necessary observations, is practically inappreciable, as the average loss was found to be less than 0.3 milligram. If desired, a correction, based upon preliminary observations, may be introduced to compensate for this loss.

The necessary operations, briefly stated, are thus: —

The heating and the determination of the temperature of a body of known weight.

Weighing of the cup containing a suitable amount of water.

Determination of the initial temperature of the cup.

Introduction of the heated body into the cup, quickly followed by the introduction of an amount of cold water sufficient to maintain the initial temperature of the cup; the temperature of the cold water being observed during this operation.

Final weight of the cup and its contents determined, and the weight of cold water added determined from data obtained.

Calculation of results by use of the equation $S = \frac{ms(\theta - t)}{M(T - \theta)}$.

This method may readily be extended over a considerable range of calorimetric work. The electric heater permits the heating of the body under investigation to any temperature ordinarily desired. The body may be cooled by a suitable freezing mixture, and the initial temperature of the cup maintained by the introduction of warm water of known temperature, thus extending the range of temperatures throughout which an investigation may be carried. The specific heat of a liquid may be determined by inclosing it in a suitable vessel, the constants of which have previously been determined. Some liquid other than water may be found preferable for special work and may readily be used in the cup and cooler.

Aniline, the use of which is advocated by Mr. E. H. Griffiths,[1] has a smaller capacity for heat and a higher boiling-point than water. It would, therefore, increase both the sensitiveness of the calorimeter in measuring small quantities of heat, and the range of temperatures throughout which an investigation might be carried.

IV.

Results Obtained.

Though subject to the errors which may arise in the application of the above three calorimetric methods, the following tabulated results give, I believe, the best determinations that have yet been made of the specific heats of the metals. They are suggestive as affording a basis of comparison of the best calorimetric methods, so far as such a comparison is possible while doubt exists as to the purity of the metals employed and the accuracy of the thermometry. I have excluded results obtained by the method of cooling, together with those obtained by various other methods which have been employed to a greater or less extent, but have been shown to be unreliable. The method of cooling has retained some place in calorimetry, presumably owing to its historic interest in connection with the work of Dulong and Petit; but since its examination and rejection by Regnault, it has been generally admitted to be erroneous both in theory and practice. I have also excluded some results, notably those of Kopp, because of the fact that approximate results only were secured, and have presented only those results which have been secured by the most accurate work possible under the given conditions. No satisfactory determinations of the specific heats of the following metals could be found: Barium, cæsium, chromium, erbium, niobium, rubidium, scandium, strontium, tantalum, terbium, vanadium, ytterbium, and yttrium. The selection of the most probable values of the mean specific heats between 0° and 100° C., which are given below, has been made after a careful consideration of the determinations that have been made and their relative values in view of the nature of the metal used, the thermometry, and the accuracy of the method

[1] Philosophical Magazine (5), 39, p. 47, 1895.

as applied. The extent and accuracy of Regnault's work have naturally suggested that it should be given a leading place.

References to original sources of information are given by numbers following the names of investigators, and referring to an appended list of important papers.

Of the above results the determinations which I have made of the specific heats of bismuth and tin are probably very nearly correct values for their means for the given temperature range. These metals were supplied to me by Mr. G. A. Hulett in a chemically pure state. The bismuth was prepared by the method employed by Prof. A. Classen.[1] The tin was prepared in the following manner. Pure Malacca tin was taken. Analysis revealed traces of copper, iron, and lead. It was oxidized with nitric acid and digested for several days with strong nitric acid, washed by decantation and again digested with strong nitric acid. It was then frequently washed by decantation for a month. The oxide was then reduced with chemically pure potassium cyanide. It was used for my determinations in the form of a cast disk of metal. The aluminium used was furnished by the Pittsburg Reduction Company. By analysis it proved to be 99.9 per cent pure, the impurity being chiefly silicon. It was prepared by the Hall process.[2] The copper used was from Lake Superior, and was about 99.98 per cent pure. Not so much reliance may be placed upon the values found for gold and zinc, as the metals were not so pure as those above mentioned. The thermometers used for these determinations were three in number. That for the heater was graduated to fifths of a degree, that for the cup to twentieths of a degree, and that for the water cooler to tenths of a degree. Hundredths of a degree could readily be estimated on each in reading temperatures. All were made by Mr. H. J. Green. They were twice standardized; once by myself by comparison with Yale Observatory Standard No. 59, made by Tonnelot of Paris; again at Johns Hopkins University, under the direction of Prof. J. S. Ames, by comparison with a certified thermometer made by Gerhardt. The latter comparison was made by use of the apparatus

[1] Berichte der Deutschen Chemischen Gesellschaft, Vol. 23, 938, 1890.

[2] Aluminium, by Prof. J. W. Richards, 2d edition, p. 288, 1890.

	Observer.	Method.	Mass used and condition.	Temperature range.	Results.	Mean.
Aluminium	Regnault [1]	Mixtures	134.810g 2 % iron and traces of silicon 124.595g	97°.0– 19°.0	0.21236 0.21212	0.21224
	Tomlinson [2]	Mixtures		100°.0– 0°.0		0.21852
	Joly [3]	Condensation	5.376g cast; pure metal prepared by Professor Reynolds	100°.0– 16°.0	0.2247 0.2236 0.2242 0.2243 0.2236 0.2215	0.2236
	Naccari [4]	Mixtures	37.25g	100°.0– 0°.0	0.2156 0.2164 0.2168 0.2166	0.2164
	Mallet [5]	Melting Ice	Absolutely pure metal	100°.0– 0°.0		0.2253
	Richards [27]	Mixtures	100–200g prepared by Hall process, by analysis: Silicon 0.07 Iron trace Aluminium 99.93	100°.0– 0°.0		0.2270
	Waterman [6]	Mixtures	6.8504g cast, prepared by Hall process: 99.9 % pure, 0.1 % silicon	100°.0– 22°.0	0.21947 0.21943 0.21948	0.21946

Antimony	Regnault [7]	Mixtures	362.3g commercial metal purified	97°.0– 16°.0	0.05113 0.05037 0.05084 0.05076	0 05078
	R. Bunsen [8]	Melting Ice	3.857g cast	99°.8– 0°.0		0.0495
	Schüz [9]	Mixtures		100°.0– 20°.0	0.05077 0.05070 0.05078 0.05032 0.05041	0.05059
	Naccari [4]	Mixtures	76.6g	100°.0– 0°.0	0.05041 0.04976 0.04994	0.05031
Arsenic	Regnault [7]	Mixtures	216.18g purified by sublimation once ;		0.08163 0.08204 0.08114	0.08140
			228.02g purified by sublimation twice		0.08082 0.08136 0.08117	
	Bettendorff and Wüllner [10]	Mixtures	6.14g crystals	68°.0– 21°.0	Mean of nine determinations	0.0830
Beryllium	Humpidge [11]	Mixtures	0 66g in form of a compressed disk. Mean corrected for impurities	45°.0– 50°.0	0.4326 0.4264 0.4357	0.4453

	Observer.	Method.	Mass used and condition.	Temperature range.	Results.	Mean.
Bismuth	Regnault [7]	Mixtures	521.56g purified with nitre	98°.0– 15°.0	0.03082 0.03089 0.03082	0.03084
			555.26g purified again	99°.0– 11°.0	0.03084 0.03093	
	Bède [12]	Mixtures	Metal purified by twice melting with nitrate of potassium and cast 135.00g 101.00 92.25 100.07	102°.0– 9°.0	0.02927 0.02981 0.02997 0.03010	0.02979
	Schüz [9]	Mixtures		100°.0– 20°.0	0.03119 0.03155	0.03137
	Waterman [6]	Mixtures	4.891g cast	100°.0– 22°.0	0.03033 0.03032 0.03039	0.03035
Cadmium	Regnault [7]	Mixtures	439.19g	98°.0– 12°.0	0.05695 0.05673 0.05639	0.05669
	R. Bunsen [8]	Melting Ice	1.867g cast	99°.8– 0°.0		0.0548
	Schüz [9]	Mixtures		100°.0– 20°.0	0.05638 0.05698 0.05661 0.05596 0.05705 0.05720	0.05669

Cadmium	Naccari [4]	Mixtures	101.65g	100°.0– 21°.0	0.05618 0.05576 0.05611 0.05595	0.0560
Calcium	R. Bunsen [8]	Melting Ice	0.2823g electrolytically prepared from pure chloride of calcium	99°.78– 0°.0	0.1722 0.1686	0.1704
Cerium	Hillebrand [13]	Melting Ice	2.0935g	100°.0– 0°.0	0.04613 0.04554	0.04583
Cobalt	Regnault [7]	Mixtures	87.87g	99°.0– 11°.0	0.10629 0.10784 0.10685	0.10710
			164.65g	97°.0– 8°.0	0.10707 0.10772 0.10682	
Copper	Regnault [7]	Mixtures	314.77g	98°.0– 15°.0	0.09537 0.09546 0.09497 0.09480	0.09515
	Bède [12]	Mixtures	72.28g fragments	100°.0– 15°.0	0.09430 0.09200 0.09364	0.09331
	Tomlinson [2]	Mixtures		100°.0– 0°.0		0.09332
	Schüz [9]	Mixtures		100°.0– 20°.0	0.09307 0.09278 0.09334	0.09306

	Observer.	Method.	Mass used and condition.	Temperature range.	Results.	Mean.
Copper	Waterman [6]	Mixtures	99.98% pure; thin bar of drawn metal { 10.9322g / 23.6625	100°.0– 23°.0	0.09475 0.09470 0.09467 0.09474	0.09471
	Naccari [4]	Mixtures	131.7g	100°.0– 17°.0	0.09341 0.09400 0.09340	0.09360
Didymium	Hillebrand [13]	Melting Ice	1.844g	100°.0– 0°.0	0.04649 0.04557	0.04603
Gallium	Berthelot [14]	Mixtures	About 34g liquid	119°.0– 13°.0 106°.0– 12°.5		0.0802
Gold	Regnault [7]	Mixtures	471.19g granulated, refined	98°.0– 12°.0	0.03250 0.03238	0.03244
	Violle [15]	Mixtures	Pure	100°.0– 0°.0		0 03160
	Waterman [6]	Mixtures	Nearly pure; in a thin bar, 17.8292g	100°.0– 24°.0	0.03066 0.03065 0.03074	0.03068
Indium	R. Bunsen [8]	Melting Ice	1.1514g	99°.82– 0°.0	0.0574 0.0565	0.05695
Iridium	Regnault [16]	Mixtures	262.78g	99°.0– 18°.0	0.03246 0.03273	0.03259
	Violle [15]	Mixtures		100°.0– 0°.0		0.0323

Iron	Regnault [7]	Mixtures	In the form of soft wire, 316.66g	98°.0– 19°.0	0.11362 0.11322 0.11373	0.11379
			Tempered wire, 293.69		0.11284 0.11398	
	Bède [12]	Mixtures	77.56g fragments	99°.2– 15°.5	0.11334 0.11120 0.11236	0.11230
	Nichol [18]	Mixtures		100°.0– 15°.0	0.1127 0.1154 0.1158 0.1168	0.11520
	Tomlinson [2]	Mixtures		100°.0– 0°.0		0.11302
	Naccari [4]	Mixtures	116.67g	100°.0– 15°.0	0.1114 0.1119 0.1122 0 1119	0.1119
Lanthanum	Hillebrand [13]	Melting Ice	0 8911g 1.682	100°.0– 0°.0	0.04582 0.04692	0.04637
Lead	Regnault [7]	Mixtures	526.33g assayed	98°.0– 13°.0	0.03134 0.03177 0.03109 0.03137	0.03140
			560.52 Spanish, very pure		0.03145 0.03129 0.03150 0.03133	

	Observer.	Method.	Mass used and condition.	Temperature range.	Results.	Mean.
Lead	Bède [12]	Mixtures	138.49g fragments	108°.0– 14°.0	0.03108 0.03154 0.03046	0.03103
	Tomlinson [2]	Mixtures		100°.0– 0°.0		0.03151
	Joly [3]	Condensation	89.508g cast	16°.0–100°.0	0.03091 0.03093	0.03092
	Schüz [9]	Mixtures	Chemically pure	100°.0– 20°.0	0.03177 0.03166	0.03171
	Naccari [4]	Mixtures	160.2g 103.2	100°.0– 15°.0	0.03082 0.03058 0.03084	0.03075
Lithium	Regnault [16]	Mixtures	0.945g	99°.0– 26°.0	0.9412 0.9405 0.9407	0.94080
Magnesium	Regnault [16]	Mixtures	91.87g 92.22	98°.0– 23°.0	0.2466 0.2533	0.24990
Manganese	Regnault [7]	Mixtures	54.98g, mean corrected for impurities	97°.0– 14°.0	0.1207 0.1227	0.1140
Mercury	Regnault [7]	Mixtures	Purified by distillation, 480.01g In glass tube, 558.58	97°.0– 12°.0	0.03318 0.03336 0.03343	0.03332
	Winkelmann [19]	Mixtures		20°.0– 50°.0		0.03330

Molybdenum	Regnault [7]	Mixtures	Agglomerated mass, 65.83g 64.23	98°.0– 12°.0	0.07254 0.07182	0.07218
Nickel	Regnault [7]	Mixtures	132.68g	99°.0– 14°.0	0.10874 0.10837 0.10878	0.10863
Osmium	Regnault [16]	Mixtures	204.59g	98°.0– 19°.0		0.03113
Palladium	Regnault [16]	Mixtures	293.37g, plate 3 mm. thick, containing slight traces of gold	98°.0– 14°.0	0.05974 0.05893 0.05916	0.05928
	Violle [20]	Mixtures		100°.0– 0°.0		0.0592
Platinum	Regnault [7]	Mixtures	569.01g pure	99°.0– 12°.0	0.03279 0.03246 0.03228 0.03223 0.03238 0.03268 0.03263	0.03243
	Violle [21]	Mixtures	Pure metal from Sainte-Clare Deville	100°.0– 0°.0		0.0323
	R. Bunsen [8]	Melting Ice		100°.0– 0°.0		0.03234
	Tomlinson [2]	Mixtures		100°.0– 0°.0		0.03261
	Joly [8]	Condensation	34.764g rolled	100°.0– 14°.0	0.0326 0.0328 0.0327 0.0328 0.0331 0.0328 0.0330	0.0328

	Observer.	Method.	Mass used and condition.	Temperature range.	Results.	Mean.
Platinum	Schüz [9]	Mixtures		100°.0– 20°.0	0.03298 0.03292	0.03295
Potassium	Schüz [9]	Mixtures		−78°.5– 23°.0		0.1662
Rhodium	Regnault [16]	Mixtures	47.107g	97°.0– 10°.0	0.05742 0.05865	0.05803
Ruthenium	R. Bunsen [8]	Melting Ice	1.7927g	99°.6– 0°.0		0.0611
Silicon	Regnault [16]	Mixtures	78.7g cast	99°.0– 22°.0	0.1732 0.1767	0.1750
	H. F. Weber [22]	Melting Ice	1.123g small brilliant gray crystals	101°.0– 0°.0		0.1795
Silver	Regnault [7]	Mixtures	345.66g	99°.0– 13°.0	0.05739 0.05691	0.05701
			496.72		0.05685 0.05679 0.05712	
	R. Bunsen [8]	Melting Ice	3.63g cast	100°.0– 0°.0		0.0559
	Naccari [4]	Mixtures	91.35g	99°.0– 23°.0	0.05581 0.05631 0.05641	0.05618
	Humpidge [11]	Mixtures			0.05677 0.05568 0.05553	0.05600

Silver	Tomlinson [2]	Mixtures		100°.0– 0°.0		0.05684
	Joly [5]	Condensation	4.027g pure rolled, prepared by Professor Reynolds	79°.0– 12°.0	0.0583 0.0571 0.0569	0.0574
Sodium	Regnault	Mixtures		–79°.5– 17°.0		0.2830
	Schüz [9]	Mixtures		–28°.0– 6°.0		0.2934
Thallium	Regnault [16]	Mixtures		100°.0– 17°.0		0.03355
Thorium	Nilson [23]	Melting Ice		100°.0– 0°.0		0.02757
Tin	Regnault [7]	Mixtures	460.65g pure	99°.0– 13°.0	0.05624 0.05652	0.05623
			462.74		0.05619 0.05622 0.05601	
	Bède [12]	Mixtures	51.01g cast	99°.0– 15°.0	0.05414 0.05475	0.05445
	R. Bunsen [8]	Melting Ice	3.0017g	99°.6– 0°.0		0.0559
	Tomlinson [2]	Mixtures		100°.0– 0°.0		0.05592
	Schüz [9]	Mixtures	Chemically pure metal	100°.0– 20°.0	0.05573 0.05554	0.05563
	Waterman [6]	Mixtures	8.3556g chemically pure, cast	100°.0– 24°.0	0.05453 0.05455 0.05451	0.05453
Titanium	Nilson and Pettersson [24]	Melting Ice	0.4468g	100°.0– 0°.0	0.1127 0.1126 0.1121	0.11250

	Observer.	Method.	Mass used and condition.	Temperature range.	Results.	Mean.
Tungsten	Regnault [7]	Mixtures	420.8g crystalline	98°.0– 12°.0	0.03358 0.03326	0.03342
Uranium	Blümcke [25]	Melting Ice	1.887g to 3.7999g	98°.0– 0°.0		0.0280
Zinc	Regnault [7]	Mixtures	247.61g distilled 284.69 293.65	99°.0– 14°.0	0.09589 0.09528 0.09548	0.09555
	Bède [12]	Mixtures	70.7g fragments	101°.0– 16°.0	0.09137 0.09059 0.09068	0.09088
	R. Bunsen [8]	Melting Ice	2.51g cast	100°.0– 0°.0		0.09350
	Tomlinson [2]	Mixtures		100°.0– 0°.0		0.09383
	Joly [3]	Condensation	48.3g cast	14°.0–100°.0	0.09434 0.09421 0.09434 0.09453 0.09443	0.09437
	Schüz [9]	Mixtures		100°.0– 20°.0	0.09676 0.09595	0.09635
	Waterman [6]	Mixtures	20.3805g, a thin cast bar, nearly pure	100°.0– 23°.0	0.09547 0.09544 0.09549	0.09547
Zirconium	Mixter and Dana [26]	Melting Ice		100°.0– 0°.0		0.0660

constructed by Professor Rowland for testing the thermometers used in his determinations of the mechanical equivalent of heat.[1] Their correction factors were thus accurately determined and the thermometers proved very satisfactory in all respects. The thermometer used for the cup remaining constantly at room temperature, and that used for the water cooler constantly at the temperature of the water, up to the point read, no variation due to stem exposure could occur. In the case of the thermometer used for the heater especial care was taken to secure accurate determinations of temperatures. As the usual correction for stem exposure was applied ($R' = R + 0.000156\, n\,(R - s)$), it was desirable to check these values in order to avoid any uncertainty as to the reliability of such a correction under the given conditions. For this purpose a platinum thermometer, consisting of a spiral of platinum wire 0.2 mm. in diameter, mounted upon strips of mica, was introduced into the heater. The metal used and the mercurial thermometer could thus be introduced into the heater as before, as the platinum spiral left the central portion of the tube unoccupied. Temperatures obtained by the mercurial thermometer, corrected for stem exposure, could thus be compared with the temperatures obtained by the use of the platinum thermometer in the manner described by Professors Callendar and Griffiths.[2] By this method it was found that the mercurial thermometer used in the heater, when corrected for stem exposure, gave temperature readings sufficiently accurate and within the limits of probable error from other sources. Weighings were made upon a Sartorius balance sensitive to one-tenth milligram under the given load. In the calculation of results, s, the specific heat of the pure water used, was taken as unity for the given temperature range. An examination of the results obtained by use of my calorimeter will demonstrate the low probable error of their mean. The results obtained are as follows: —

[1] Proceedings of the American Academy of Arts and Sciences, Vol. 7, p. 90, 1879–80.
[2] L. E. and D. Philosophical Magazine (5), Vol. 32, p. 104, 1891.

	M	t	θ	T	m	S
	grams	degrees	degrees	degrees	grams	
Bismuth .	4.891	0.20	22.32	99.71	0.519	0.03033
		0.20	22.65	100.15	0.512	0.03032
		0.25	22.45	100.10	0.520	0.03039
					Mean	0.03035
Tin . . .	8.3556	0.20	22.75	100.06	1.562	0.05453
		0.20	24.20	100.16	1.4425	0.05455
		0.20	24.15	99.96	1.4416	0.05451
					Mean	0.05453
Aluminium	6.8504	0.20	22.04	100.02	5.367	0.21943
		0.20	22.58	99.86	5.194	0.21947
		0.20	21.88	100.07	5.423	0 21948
					Mean	0.21946
Copper . .	10.9322	0.19	23.39	100.00	3.4204	0.09475
		0.30	22.42	100.20	3.6403	0 09470
	23.6625	0.25	23.62	99.80	7.3020	0.09467
		0.30	21.51	100.00	8.2960	0.09474
					Mean	0.09471
Gold. . .	17.8292	0.20	24.00	100.00	1.7456	0.03066
		0.35	24.41	100.00	1.7101	0.03065
		0.35	23.45	99.95	1.8153	0.03074
					Mean	0.03068
Zinc . . .	20.3805	0.20	23.40	99.90	6.4160	0.09547
		0.20	23.50	100.00	6.3860	0.09544
		0.27	23.85	100.20	6.3017	0.09549
					Mean	0.09547

The selection of the probable values of the mean specific heats of the metals between 0° and 100°, from the tabulated results, is difficult in view of the considerations which have been stated. In the case of those metals of which but one presumably creditable determination has been made, that one has been given provisionally. In the case of the metals which have been subject to several creditable determinations, the attempt has been made to select the values best sustained. It will be observed that in this selection greater weight has been given to results obtained by the method of mixtures than to those obtained by the method of con-

densation, or the method of melting ice. This preference is due partly to the sources of error, which may exist in the latter methods, and partly to the fact that, judging by results, those obtained by use of the method of mixtures seem to be best sustained. We may judge of the accuracy of the method of condensation by the work of Dr. Joly, but it has not been generally used and we are unable to determine what concordance there might be in the work of various investigators employing this method. We have more data for the examination of the results obtained by the method of melting ice, however, and such an examination may be desirable. A comparison may readily be made by reference to the determinations made of the specific heats of platinum, silver, and zinc, for which all three methods have been employed. It is seen that, although some variations exist in the values found by the method of mixtures as employed by different investigators, they are very evidently higher than those obtained by the method of melting ice as applied by use of Bunsen's ice calorimeter. The values found by use of the method of condensation by Dr. Joly are also higher than those obtained by the Bunsen calorimeter. It is improbable that the results obtained by so many skillful investigators, applying the method of mixtures with considerable variations at different times, their results sustained by an entirely different method, that of condensation, should be incorrect, while those obtained by the few investigators who have used the Bunsen ice calorimeter should be correct. Exception might be taken to this statement by citing the case of the results obtained for the specific heat of aluminium, among which Professor Mallet's determination, made by use of the Bunsen calorimeter, has a high value. This is readily explained, however, as nearly all of the aluminium used has contained considerable traces of silicon, which has lowered the value, while Professor Mallet's determination was made by use of chemically pure aluminium, prepared for the determination of its atomic weight.

Considerable weight should be given to a low probable error of the mean of a series of determinations. Other things being equal, it naturally gives greater confidence in the result. In the case of

results obtained by use of the Bunsen calorimeter, it is difficult to find material from which to determine the probable error of the mean values given, as most investigators who have used this method seem to be unwilling to publish more than their final values.

The fact that the specific heats of most metals increase as their temperatures rise leads us to another consideration; namely, whether determinations made at temperatures varying greatly as to their proximity to the melting-points of the various metals, are properly comparable. This can be made clear only by the work of those investigators who have examined the variations in the specific heats of the metals up to their melting-points. For this reason I shall not enter into the matter in the following comparison.

It will be observed that if we select a few of the specific heats most probably accurate, namely, those of aluminium, 0.2236; bismuth, 0.0303; copper, 0.0947; gold, 0.0316; iron, 0.1130; lead, 0.0310; platinum, 0.0326; silver, 0.0574; and tin, 0.0545, and multiply by the atomic weights corresponding, the mean of the atomic heats thus formed is 6.2444.

The mean atomic heat of the whole series is slightly lower than this value.

Metals.	Temperature range.	Specific heats.	Atomic weights.	Atomic heats.
	degrees			
Aluminium	100.00–16.0	0.2236	27.1	6.0595
Antimony	100.00– 0.0	0.0505	120.0	6.0600
Arsenic	68.00–21.0	0.0830	75.0	6.2250
Barium				
Beryllium	45.00–50.0	0.4453	9.0	4.0077
Bismuth	100.00–22.0	0.0303	208.0	6.3024
Cadmium	100.00–00.0	0.0565	112.0	6.3280
Cæsium				
Calcium	99.78–00.0	0.1704	40.0	6.1860
Cerium	100.00–00.0	0.0458	140.0	6.4120
Chromium				
Cobalt	99.00–11.0	0.1071	58.5	6.2653
Copper	100.00–23.0	0.0947	63.6	6.0429
Didymium	100.00–00.0	0.0460	146.6	6.7436
Erbium				

Metals.	Temperature range.	Specific Heats.	Atomic weights.	Atomic heats.
	degrees			
Gallium	106.00–12.5	0.0802	70.0	5 6140
Gold	100.00–00.0	0.0316	198.0	6.2468
Indium	99.82–00.0	0.0569	113.0	6.4297
Iridium	100.00–00.0	0.0324	193.0	6.2532
Iron	100.00–00.0	0.1130	56 0	6.3280
Lanthanum	100.00–00 0	0.0463	138.0	6.3894
Lead	100.00–00.0	0.0310	206.0	6.2006
Lithium	99.00–26.0	0.9408	7.0	6.5856
Magnesium	98.00–23.0	0.2499	24.4	6.0975
Manganese	97.00–14.0	0.1140	55.0	6.2700
Mercury	97.00–12.0	0.0333	200.0	6.6600
Molybdenum	98.00–12.0	0.0721	96.0	6.9216
Nickel	99.00–14.0	0.1086	58.5	6.3531
Niobium				
Osmium	98 00–19.0	0.0311	191.0	5.9301
Palladium	100.00–00.0	0.0592	106.0	6.2752
Platinum	100.00–00.0	0.0326	196.0	6.3896
Potassium	−78.50–23.0	0.1662	39.0	6.4818
Rhodium	97.00–10.0	0.0580	104.0	6.0320
Rubidium				
Ruthenium	99.60–0.00	0.0611	103.0	6.2933
Scandium				
Silicon	101.00–0.00	0.1795	28.4	5.0978
Silver	79.00–12.0	0.0574	108.0	6.1992
Sodium	−79.50–17.0	0.2830	23.0	6.5090
Strontium				
Tantalum				
Terbium				
Thallium	100.00–17.0	0.0335	204.0	6.8340
Thorium				
Tin	100.00–24.0	0.0545	118.0	6.4310
Titanium	100.00–00.0	0.1125	48.0	5.4000
Tungsten	98.00–12.0	0.0334	184.0	6.1456
Uranium	98.00–00.0	0.0280	240.0	6.7200
Vanadium				
Ytterbium				
Yttrium				
Zinc	99.00–14.0	0.0955	65.0	6.2075
Zirconium	100.00–00.0	0.0660	90.0	5.9400

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EXPERIMENTAL DETERMINATIONS OF THE TEMPERATURE IN GEISSLER TUBES.

By R. W. Wood.

§ 1. The opinion that the temperature of the gas in the positive part of the discharge in Geissler tubes lay far below the red heat was first expressed by E. Wiedemann,[1] and Hittorf[2] was led to the same conclusion from simple experiments. The theoretical calculations of the temperature in the unstratified anode light by Warburg[3] yielded similar results. Hittorf[4] showed, further, that the temperature in the negative light lay at least below the melting point of platinum, for at this temperature the luminosity of the gas disappeared entirely.

Calorimetric observations have been made by Paalzow and Neesen[5] and others, which give some idea of the total heat production, but as far as I know no accurate measurements have been made of the temperature of the gas in different parts of the discharge. It is clear that such measurements must be made in the discharge of a constant battery, and not in the intermittent discharge of an induction coil.

The prime object of this investigation has been to obtain the relative temperatures in different parts of the discharge, with especial reference to the stratifications. Owing to the narrow space limits between which it was necessary to work in the stratified discharge, a bolometer, consisting of a loop or spiral of very fine platino-iridium wire, appeared to be the most suitable measuring instrument.

§ 2. The constant current for producing the discharge in the vacuum tube was furnished by a high potential accumulator bat-

[1] E. Wiedemann, Wied. Annalen, 6, p. 298, 1879.
[2] W. Hittorf, Wied. Annalen, 7, p. 577, 1879.
[3] E. Warburg, Wied. Annalen, 54, p. 265, 1895.
[4] W. Hittorf, Wied. Annalen, 21, p. 123, 1884.
[5] H. Paalzow and F. Neesen, Wied. Annalen, 56, p. 276, 1895.

tery of 600 cells, the electromotive force being about 1250 volts. A Hittorf resistance tube, with a movable electrode filled with a solution of cadmium iodide for regulating the current strength, and a Siemens & Halske direct-reading torsion galvanometer for measuring the current, were introduced into the circuit.

§ 3. Before commencing work with the bolometer, a preliminary investigation was made on the rise of pressure within the tube due to the discharge, and from this pressure increment the corresponding temperature increment was calculated. Hittorf speaks of using one of his tubes as an air thermometer, and of the very slight expansion of the gas due to the heating, but he gives no numerical results. The change of pressure being too slight to be accurately measured by means of a mercurial manometer, sulphuric acid was used in place of the heavier fluid. The apparatus is shown in Fig. 1, and consists of a small glass flask *A*, into the neck of which is fused a vertical tube, which passes to the bottom and communicates above with the discharge tube *B*. The flask contains a little sulphuric acid, and the space above the liquid is also in communication with the discharge tube through the lateral tube, which is furnished with a stopcock. By this arrangement the pressure above the liquid can be made just sufficient to support a short column of acid in the vertical tube, the cock being opened during the process of exhaustion and closed a few minutes before the requisite vacuum is reached, the further exhaustion causing a rise of the fluid. On closing the cock between the tube and the pump, and turning on the current, a fall of the column is immediately noticed, and by measuring this the increase of pressure and consequently of temperature can be determined from the formula

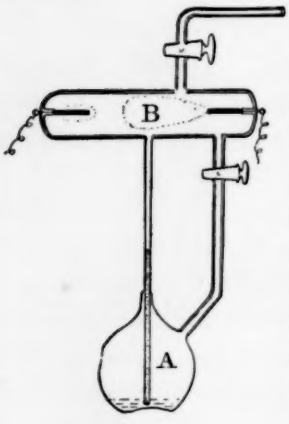

Fig. 1.

$$t - t_0 = \frac{p - p_0}{p_0}(272.5 + t_0).$$

The temperature at the start was 20° and the pressure 2 mm. The passage of a current of 0.001 ampere caused a depression of

1 mm. in the H_2SO_4 barometer, corresponding to 0.135 mm. of mercury. By the formula we find that the rise in temperature, or $t - t_0$,

$$= \frac{0.135}{2}(272.5 + 20) = 19.7.$$

The change of volume in the two vessels due to the sinking of the column is vanishingly small in comparison to their volumes, and can be neglected. This method, of course, shows only the average temperature rise, and the result cannot be strictly compared with any of those found with the bolometer, which gives local temperatures.

§ 4. Warburg has shown by his calculations that in a gas at low pressure, heated by the discharge, a stationary temperature is established within a fraction of a second, so rapid is the conduction of heat. In other words, a gas is heated to its maximum, or cools to its original temperature within a small fraction of a second, on the commencement or cessation of the discharge. With an interrupted current, providing the interruptions are not too rapid, we should then expect the temperature to rise and fall exactly in time with the interrupter. Corresponding to this rise and fall of temperature there should be a rise and fall of pressure, and this I find to be the case.

The inertia of the column of acid in the apparatus last described (Fig. 1) is too great to allow the fluid to respond to these rapid changes of pressure, but I find that with the device shown in Fig. 2 they can be shown very well. This consists of a discharge tube with a rectangular U manometer, in which are two drops of sulphuric acid. The tube is connected with the pump by means of a short piece of rubber hose, and during the process of exhaustion the acid is collected into a single drop. When the desired vacuum has been reached, the drop can be separated into two by carefully tipping the tube back and forth, forming a bubble between, in which the gas is at the same pressure as that in the discharge tube. On connecting the electrodes with a Ruhmkorff coil in action, the

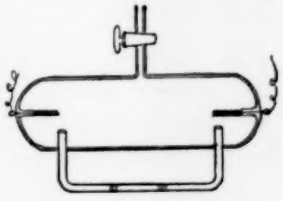

Fig. 2.

drops, which are about 3 cm. apart, alternately approach and recede, vibrating exactly in unison with the interrupter. The pressure at which this is shown to the best advantage is about 5 mm. When it is too low, the amplitude of the vibrations is too small to be observed.

§ 5. Of the measurements made with the bolometer I shall first take up those which show the relation of the rise in temperature to the current strength. In this investigation the bolometer wire was fixed in position, while in experiments to be described further on it was so arranged that it could be moved up and down within the discharge tube.

The arrangement of the apparatus is shown in Fig. 3.

In the axis of the discharge tube is mounted a spiral of very fine platino-iridium wire. The length of the wire was 2 cm., its diam-

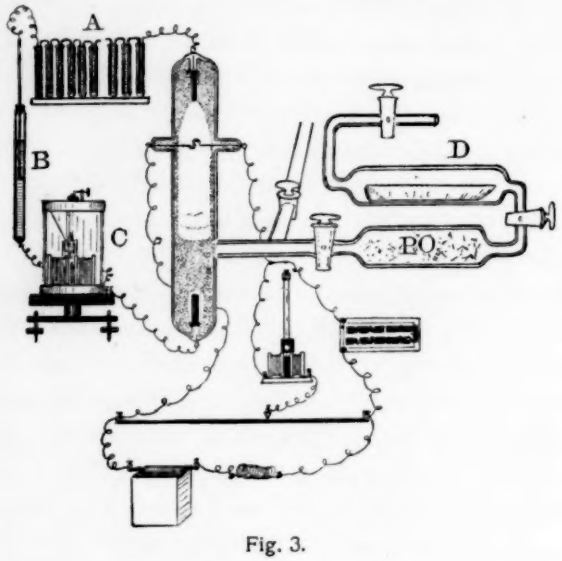

Fig. 3.

eter 0.035 mm., and the distance between the ends of the large wires which supported the spiral was 0.5 cm. The internal diameter of the tube was 1.5 cm., being the same as used by A. Herz in his research on the fall of potential in the anode light, which will be alluded to later, and on which Warburg based his calculations. The high potential battery *A*, the resistance tube *B*, and the

torsion galvanometer *C*, I have already alluded to. The bolometer was connected with a mirror galvanometer, resistance box, and Wheatstone bridge in the usual manner, as shown in the diagram, the current being furnished by a single accumulator, with a 20-ohm resistance coil in the circuit.

§ 6. Nitrogen made by passing air over heated phosphorus contained in a porcelain boat in the tube *D*, and then dried by means of phosphoric acid, was used in most of the experiments, the current in air not being steady enough to admit of accurate measurements being made.

§ 7. The apparatus was so arranged that within the temperature limits that were observed, the rise in temperature was proportional to the deflections of the galvanometer, as observed with a scale and telescope. The temperature increment corresponding to a deflection of one scale division was found by immersing the bolometer wire in warm oil with a normal thermometer reading to tenths of a degree, and allowing the oil to slowly cool. One degree was found to correspond to 4 mm. scale deflection.

§ 8. It is of course a question how nearly the wire takes the temperature of the gas. On account of radiation and conduction it must lag behind the gas, and to give absolutely correct values should be of infinite thinness. Some idea of the size of the error can be formed by working with wires of different thickness. The one used was 0.035 mm. in diameter, and since finer wire is hard to procure and difficult to manage, platinum leaf less than 0.001 mm. in thickness was used, which was furnished rolled together with silver. A strip 1 mm. wide and 1.5 cm. long was mounted in the tube in place of the spiral, the silver backing giving the necessary rigidity. The soldered joints were protected with asphalt varnish, and the silver removed with dilute nitric acid. Owing to the extreme tenuity of the remaining strip, great care was necessary in washing and drying out the tube. The resistance of the strip was found to be 2.8 ohms, which is almost identical with the value calculated for a strip of its size having a thickness of 0.001 mm. The tube was exhausted to a vacuum of 2 mm. and a current of 0.0012 ampere sent through it, the strip of platinum leaf being in the anode light. The scale deflection

was 40 cm., about ten times as large as with the wire. This was due principally to the larger temperature coefficient of the strip, which was of pure platinum, while the wire was an alloy of platinum and iridium. The strip was now immersed in oil at 25°, and the temperature was raised until a galvanometer deflection of 40 cm. scale was produced, the temperature of the oil being found to be 43°, showing a rise of 18°. The temperature rise of the gas in the anode light, under similar conditions, as measured with the wire, was 19°, as will be seen by reference to Table IV. The platinum foil took the temperature of the gas more rapidly than the wire, and would consequently have been better adapted to the experiments, were it not for the influence that the wide strip had on the uniformity of the discharge. With the fine wire this deforming action was noticeable to a certain degree, especially in working with stratified discharges with the movable bolometer, the strata appearing as though elastic, and only yielding to the wire after slight deformation. This effect will be alluded to subsequently. The similarity of results obtained with the wire and the foil justify the assumption that the wire takes the temperature of the gas nearly enough for our purpose.

§ 9. It is also necessary to make sure that the discharge within the tube can only affect the galvanometer by changing the resistance of the wire. The current was shut off from the bolometer circuit and a discharge passed through the tube, which caused no deflection, showing the absence of thermo-currents, or currents switched from the high potential discharge.

§ 10. The first sets of measurements were made in the unstratified anode light, at different pressures and with varying current strength. The cock communicating with the air pump was left open, to eliminate as much as possible the rise of pressure due to the warming of the gas. The values are given in the following tables: i being the current strength, w the temperature rise, and $\frac{w}{i}$ the ratio between these values. To avoid complicating the tables I have omitted the galvanometer deflections and given the corresponding temperatures.

TABLE I.

PRESSURE, 0.3 mm.

i	w	$\frac{w}{i}$	i	w	$\frac{w}{i}$
0.0015	13°.0	87	0.0022	18°.0	82
0.0017	15°.0	88	0.0025	19°.5	78
0.0018	15°.7	87	0.0032	22°.5	73
0.0021	17°.7	84	0.0036	25°.7	71

TABLE II.

PRESSURE, 1.8 mm.

i	w	$\frac{w}{i}$	i	w	$\frac{w}{i}$
0.0007	11°.5	164	0.0019	26°.2	138
0.0009	14°.0	155	0.0025	34°.0	136
0.0012	17°.0	142	0.0032	42°.2	132
0.0015	21°.7	145			

TABLE III.

PRESSURE, 2 mm.

i	w	w calculated by Warburg.	$\frac{w}{i}$
0.0012	19°.0	22°.0	158
0.0020	30°.0	—	150
0.0032	45°.0	40°.6	143

TABLE IV.

PRESSURE, 3 mm.

i	w	w calculated.	$\frac{w}{i}$	i	w	w calculated.	$\frac{w}{i}$
0.0010	23°.0		230	0.0022	44°.0		200
0.0012	27°.0	30°.0 Warburg	225	0.0025	49°.7		198
0.0015	31°.0		207	0.0027	50°.7		187
0.0018	37°.0		205	0.0032	59°.5	62.7 Warburg	186
0.0020	40°.0		200	0.0046	73°.0		160

It will be seen from the values w, which show the rise in degrees above the room temperature, 25°, that the views held by Wiedemann and Hittorf regarding the comparatively low temperature in the Geissler tube are corroborated. The theoretical calculations by Warburg, to which I have previously alluded, which are based on the supposition that the electrical energy consumed in a portion of the tube, and represented by the product of the current strength and the potential fall, is practically all transformed into heat, give results which agree well with the values which I have found. These calculated temperatures for the axis of the anode light are given with the observed ones in Tables III. and IV.

The bolometer wire, not coinciding with the axis of the discharge, but occupying a space 0.5 cm. wide, gives the average temperature in this space, which is found by calculation to be about $\frac{17}{18}$ of the value in the axis.

The ratio $\frac{w}{i}$ is, according to the theory of Warburg, proportional to the potential gradient. The decrease in the values, with increasing current strength, is most probably due to the fact that, the gas being at constant pressure, its density, and therefore the gradient, diminish with rising temperature. The stop-cock leading to the pump was next closed, thus keeping the gas in the tube at a constant volume and density. In this case it was found that $\frac{w}{i}$ was nearly a constant, as shown in the following tables. According to the work of Herz on potential fall, we should expect $\frac{w}{i}$ to decrease in this case also, but this did not seem to be the case.

TABLE V.

PRESSURE, 0.3 mm.

i	w	$\frac{w}{i}$	i	w	$\frac{w}{i}$
0.0015	13°.0	87	0.0026	21°.9	84
0.0017	15°.2	89	0.0029	24°.2	83
0.0020	17°.4	87	0.0034	28°.5	84

TABLE VI.

PRESSURE, 1 mm.

i	w	$\frac{w}{i}$	i	w	$\frac{w}{i}$
0.0015	19°.0	126	0.0028	34°.0	121
0.0018	21°.0	117	0.0039	48°.0	123
0.0022	26°.0	118			

§ 11. By reversing the direction of the current the bolometer was brought into the dark space which separates the positive and negative light, and a set of values obtained in this portion of the discharge with currents of varying strength. The temperature here was found to be much lower than in the anode light, and the quotient $\frac{w}{i}$ was nearly constant, indicating that in this case the potential fall was independent of the current strength. Table VII. gives the values found in the dark space.

TABLE VII.

PRESSURE, 2 mm.

i	w	$\frac{w}{i}$	i	w	$\frac{w}{i}$
0.0009	08°.7	97	0.0038	35°.7	94
0.0010	10°.2	93	0.0040	37°.5	94
0.0012	11°.5	96	0.0048	45°.0	93
0.0021	19°.5	93			

§ 12. The measurements described thus far have been for a fixed part of the discharge. The complete investigation of the temperature fluctuations in passing along the tube from anode to cathode was next undertaken.

The chief difficulty lay in devising a method of easily and rapidly moving the bolometer back and forth in the discharge without impairing the vacuum. The apparatus is shown in Fig. 4. A vertical tube A, 1 cm. in diameter and 80 cm. long (shortened in

diagram), carries on its upper end the discharge tube with its laterally placed electrodes. Through A passes a small tube C, bent in a U at the bottom and carrying on its upper end the loop D of platino-iridium wire which serves as the bolometer wire. Within C are the two insulated copper conducting wires, terminating in platinum points which are fused through the glass, and to which are soldered the terminals of the bolometer loop, which is bent into a horizontal plane by manipulation through the side tube E, subsequently joined to the pump.

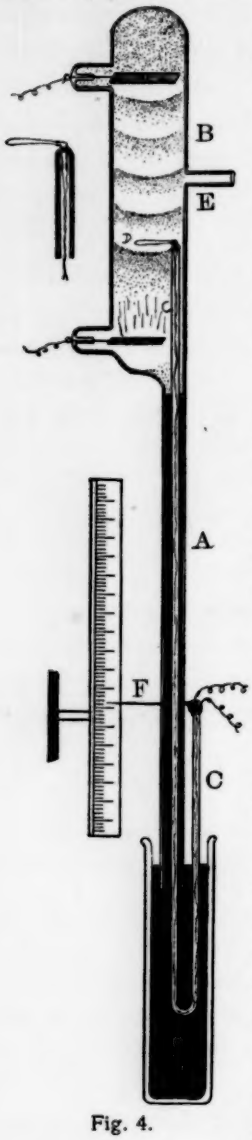

Fig. 4.

An enlarged view of the upper end of the tube carrying the bolometer is shown to the left of the discharge tube. The lower end of A is now introduced into a deep jar of mercury, and on exhausting the apparatus the fluid rises, forming a barometer column, through which the smaller tube, carrying the bolometer on its end, slides up and down. The arm of the U which projects from the mercury jar carries a pointer F, which moves along a millimeter scale and indicates the exact position of the wire loop in the discharge. All the connections were carefully soldered, otherwise changes of resistance occurred when the bolometer tube was moved. With this device it was possible to explore the entire tube from the cathode to the anode and make a complete map of the temperature changes.

§ 13. In the unstratified anode light the temperature was sometimes constant for the greater part of the column, and sometimes rose to a maximum near the middle, falling away again as the dark space was approached. This maximum was always found when the light was on the point of stratifying, and sometimes at higher

pressures. The exact conditions that determined whether the temperature had a maximum in the middle of the column or was constant for the greater part, could not be determined, but the extent of the anode light appeared to have something to do with it. Under exactly the same conditions of pressure and current strength, so far as can be determined, the light will sometimes extend much further down the tube than at others, and I could find no way of remedying this trouble, which has been observed by other experimenters.

There was always a decrease of temperature on nearing the dark space. On leaving the anode light, the temperature drops very suddenly, reaching a minimum near the middle of the dark space, and then rises again very rapidly on entering the blue negative light. The results obtained with the movable bolometer are clearer when shown by curves than when expressed in tabular form. The condition where a maximum exists in the anode light is shown in Fig. 5, the abscissæ being distances from the anode, as shown by the pointer on the scale, and the ordinates temperatures as calculated from the galvanometer deflections. The room temperature (26°) is shown by the horizontal line, and the character of the discharge and its position on the scale indicated by the drawing beneath. The pressure was about 1.5 mm. and the current strength 0.001 ampere. A series showing constant temperature in the anode light is shown in the upper curve in Fig. 6, the position of the boundary between the positive light and the dark space being indicated.

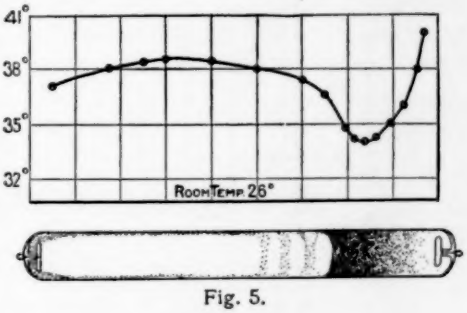

Fig. 5.

§ 14. When the pressure in the tube is sufficiently reduced to cause the appearance of stratifications in the anode light, a maximum in the middle of the column is always to be found, the temperature rising as we recede from the anode, and falling again after the middle of the column is passed. In addition to

this there is a periodic rise and fall, the light disks being warmer than the dark spaces between them, although one often finds a point where there is no change of temperature on passing from a light space to a dark. The cause of this is at once apparent when

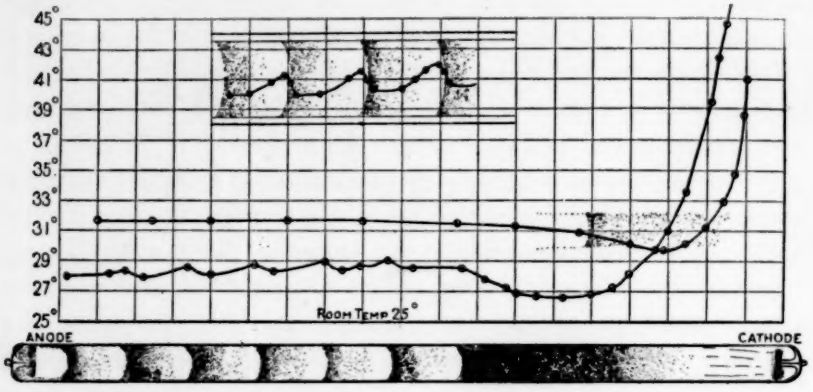

Fig. 6.

the results are plotted on coördinate paper, the decrease due to the passage from light to dark being compensated by the increase due to approach to the maximum point (Fig. 7).

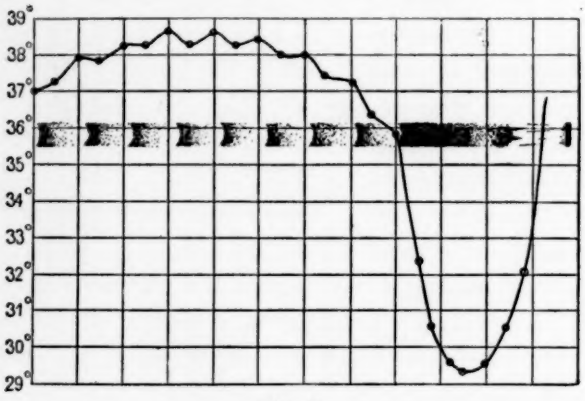

Fig. 7.

Lehmann[1] came to the conclusion that in the stratified discharge the temperature of the light spaces was higher than that of the dark. By mixing oil vapor with the gas, he observed that the car-

[1] O. Lehmann, Zeitschrift für Electrochemie, 21 and 22, 1896.

bon particles set free glowed in the light spaces, but were invisible in the dark. If this luminosity of the carbon was true incandescence caused by the high temperature of the gas, the conditions of current strength and pressure must have been very different from any that I have investigated, since in no case have I found the temperature to be over 100°.

The curve showing the temperature fluctuations in the stratified discharge at low pressure (0.1 mm.) is shown in Fig. 6 (lower curve), the straight line showing the room temperature, and the drawing beneath indicating the character and position of the discharge with reference to the curve. The maximum in the anode light is not as marked as it is at higher pressure, owing to the smaller changes of temperature. In Fig. 7, which is for a pressure of 0.5 mm., it is very evident, as is the existence of two spots, one on each side of the maximum, where there is no change on going from a light to a dark space.

A careful set of observations was made of the periodic change in the stratified anode light, five points being taken for each cylinder of light.

The results are shown for three consecutive disks in Fig. 6 in the small drawing above the curves. The conditions are the same as in the tube represented below, only the ordinates are taken on a larger scale, and more points are taken.

The temperature is steady for a certain distance, then rises gradually to a maximum, situated in the brightest part of the disk,

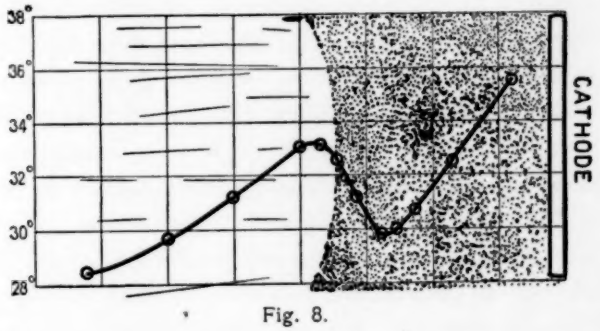

Fig. 8.

turns and drops suddenly as we pass out of the sharply defined edge of the disk. The difference in temperature between the

light and dark spaces varies from 0°.5 to about 1°.5, depending on the degree of exhaustion and current strength.

§ 15. Assuming that the electrical energy is wholly converted into heat, these temperature curves *should* resemble closely the curves representing the potential fall in different parts of the discharge. At the present time no very accurate maps have been made of the potential fall between the anode and cathode. What is already known agrees with the results found in this investigation, which may be expressed thus:

Positive light . . .	Medium potential fall . . .	Medium temperature.
Dark space	Small potential fall	Low temperature.
Negative light . . .	Large potential fall	High temperature.

§ 16. It may not be out of place to mention here one or two phenomena that were observed in working with stratified discharges, though they have no direct bearing on the subject. Though in general the bolometer wire passes through the strata cleanly without moving them or altering their position, at certain pressures I find that the wire drags the stratum through which it is passing (moving from + to − electrode) into the one immediately below it, the two dissolving into one. At this moment, however, a new stratum springs off the anode, so that as we work down the tube dragging each stratum in succession into its neighbor, the total number remains always the same.

Another effect to which I have alluded before, is the apparent resistance which the sharply defined edges of the strata offer to the penetration of the wire. The edge acts as if it had an elastic skin, or a sort of surface tension, bending in as the wire pushes against it, and finally snapping back to its original position, leaving the wire well within the luminous disk. Too little is known about the strata to make any discussion of these two facts worth while, and I merely record them without comment.

§ 17. A few experiments were made with hydrogen, but owing to the difficulty of maintaining a steady current in this gas, they were not carried very far. The fact was established, however, that under similar conditions of pressure and current strength the heating was only about 11 per cent of that found in the case of nitro-

gen, this being due to the fact that the potential fall is less, and also to the fact that hydrogen is a much better conductor of heat than nitrogen. With hydrogen at 1.8 mm. pressure, with a current of 0.0015 ampere, a rise of temperature of only 2°.5 was observed. Referring to Table II., the rise obtained for nitrogen under similar conditions was 21°.7, about nine times as great. Warburg calculated the temperature rise for hydrogen at 5 mm. with a current strength of 0.001 to be 4°.1, and for nitrogen under nearly similar conditions 41°.3, or ten times as great.

§ 18. While working with hydrogen at very low pressures, I found evidence of a fall of temperature on passing from the negative light into the Crookes dark space, and have found mention made of this by Wiedemann,[1] who worked with a thermo-element applied to the outside of the tube. It is only to be found when the length of the dark space is considerable; at higher pressures, if it exists at all, it is completely masked by the very rapid rise in temperature on approaching the cathode. This was also noticed by Wiedemann. This same temperature minimum was found in nitrogen by subsequent trials.

It is not always to be found, however, even with hydrogen. One tube with comparatively small rectangular electrodes, showed it very distinctly (Fig. 8), while another, with large aluminium plates, gave no indication of it. In the latter tube the Crookes dark space was more or less filled with blue negative light, which may have accounted for the absence of the minimum. It will be interesting to see whether future measurements of the potential fall in this part of the discharge show a corresponding minimum.

§ 19. Commenting in general on the results found in this investigation, I consider the curves obtained with the movable bolometer to indicate the relative temperatures in different parts of the discharge with considerable accuracy. As to the results found with the stationary wire and variable current strength, the irregularity of the series $\frac{W}{i}$ shows that there is a source of error somewhere. This, I think, may be the instability of the conditions in the tube, such as the varying length of the anode light, to which I

[1] E. Wiedemann, Annalen, 20, p. 775, 1883.

have already alluded. The values may, however, be considered correct to within two or three degrees, I think. They agree well with theory, though a too strict comparison cannot be made on account of the probable convection currents in the tube and the radiations from the always more or less warm cathode.

I have, in concluding, to thank Professor Warburg for the kind interest that he has taken in the progress of the work.

BERLIN, PHYSICAL INSTITUTE OF THE UNIVERSITY.

THE VISCOSITY OF MERCURY VAPOR.[1]

By A. A. Noyes and H. M. Goodwin.

THE uncertainty which attaches to the specific heat ratio of gases as a means of distinguishing between monatomic and polyatomic molecules has been recently made evident by the extended discussions of the significance of that property in connection with the atomic weights of argon and helium. It is therefore of great interest to investigate other properties which may be expected to be related to the atomicity of the molecule. Of such properties those dependent on the volume or cross-section of the molecules seem most promising. We have therefore undertaken the investigation of one of these, the viscosity or internal friction, in order to determine whether a marked difference in its value exists in the case of gases with monatomic and those with polyatomic molecules. To this end we have made comparative measurements of the viscosity of hydrogen, carbon dioxide, and mercury vapor at the boiling temperature of the last-named substance.

According to the kinetic theory of gases, the viscosity coefficient has the theoretical significance expressed by the following equation[2]:

$$\eta = \frac{1}{\pi} NmLc,$$

in which N is the number of molecules in the unit of volume, m the mass of a single molecule, L the mean free path, and c the mean velocity. Moreover, the free path L is dependent solely on the number of molecules N and the mean cross-section q of a single molecule, or of its sphere of action[3]:

$$L = \frac{1}{4\sqrt{2}Nq};$$

[1] Read at the Buffalo meeting of the American Association for the Advancement of Science, August 25, 1896, and at the meeting of the American Academy of Arts and Sciences, October 14, 1896.

[2] O. E. Meyer, Kinetische Theorie der Gase, 1st ed., 130, 139.

[3] O. E. Meyer, Kinetische Theorie der Gase, 206, 218. The symbol Q used by the author represents the total cross-section of all the molecules in the unit of volume, and is therefore evidently equal to Nq.

whence it follows that

$$\frac{1}{4\pi\sqrt{2}} = \frac{mc}{q};$$

or, for any two different gases,

$$\eta_1 : \eta_2 = \frac{m_1 c_1}{q_1} : \frac{m_2 c_2}{q_2}.$$

But, since for any two gases at constant temperature,

$$m_1 c_1^2 = m_2 c_2^2,$$

the above proportion may be simplified to the following equation:

$$\frac{q_1}{q_2} = \frac{\eta_2}{\eta_1}\sqrt{\frac{m_1}{m_2}}, \qquad (1)$$

from which it is evident that the relative mean cross-sections of the molecules of the two gases are readily calculated from their molecular weights and viscosity coefficients. It was thought by us that monatomic molecules might prove to be much smaller than polyatomic ones, since it seems *a priori* not improbable that the spaces between the atoms of the latter are large in comparison with the dimensions of the atoms themselves. The experiments to be here described show, however, that no marked distinction exists between monatomic and polyatomic gases in this respect.

Experiments on the viscosity of mercury vapor, and especially on the effect of temperature upon it, have been made already by S. Koch,[1] who calculated that at 300° the volume of the mercury molecule is 4.4 as great as that of the hydrogen molecule. As this calculation was not based on direct comparative experiments made by passing the two gases through the same capillary, but was an indirect one involving the measurements of different experimenters and the dimensions of the capillaries used by them, it seemed desirable to subject the matter to further investigation in the direct manner indicated. Moreover, the author does not discuss the significance of his result in its bearing on the relative magnitude of atoms and molecules.

[1] Wied. Ann. 19, 857, 1883.

The method used by us in determining the relative viscosity consisted in measuring the quantities of the different gases which, under a constant difference of pressure, passed in a given time through the same capillary kept at a definite constant temperature. O. E. Meyer[1] has derived the following formula for calculating the viscosity coefficient of a gas from its rate of flow through a capillary tube:

$$\eta = \frac{\pi}{16} \frac{R^4}{\lambda} \frac{(p_1^2 - p_2^2)t}{p_1 V_1},$$

where λ is the length and R the radius of the tube, t the time, p_1 the pressure at which the gas enters, and p_2 that at which it leaves the tube, and V_1 the volume of the transpired gas measured at the pressure p_1. In case of comparative experiments made with the same capillary on two different gases, the following proportion holds true:

$$\eta_1 : \eta_2 = \frac{(p_1^2 - p_2^2)_1 t_1}{n_1} : \frac{(p_1^2 - p_2^2)_2 t_2}{n_2}, \qquad (2)$$

in which n_1, n_2 represent respectively the number of gram molecular weights of the two gases transpired (since n is proportional to the product pV).

The apparatus and experimental method that we employed were necessarily quite different from the usual ones, and they will therefore be briefly described. The capillary used in the most complete series of experiments consisted of a glass tube about 74 cm. in length and 0.34 mm. in internal diameter (determined by measuring the volume of a known length by means of mercury). A smaller capillary about 49 cm. in length and 0.22 mm. in diameter was used in a preliminary series. The capillary was bent in the manner shown in Fig. 1, except that as actually constructed it was made much more compact. To its ends were fused pieces of ordinary glass tube, as shown in the figure; one of these was provided at the point A with a ground glass joint. The capillary was placed in a vertical position in a heavy steel cylinder A (Fig. 2) (30 cm. high, 2.8 cm. internal diameter), having a small orifice at the side, through which the ground joint protruded for a distance

[1] Pogg. Ann. 127, 269.

of about one centimeter. The capillary was held in position in the orifice by packing with loose asbestos. Although the capillary was vertical, the influence of gravity was eliminated by reason of the fact that the ascending and descending parts were made equal in length. The top of the cylinder was closed by an iron plate screwed down with a nut *N*. The nut and the plate were perforated in the center, and into the latter was welded an open iron tube *B*, projecting upwards, 25 cm. in length and 1.5 cm. in diameter. The cylinder was completely covered, except on the bottom, with a jacket of asbestos, about 5 cm. thick, and the projecting tube *B*, which was to serve as a condenser, was wound with spirals of copper wire to increase the cooling surface. Pure mercury was placed in the cylinder and boiled vigorously by means of a number of lamps beneath. The capillary was thus kept at the boiling temperature of mercury under atmospheric pressure. No regard was paid to the variations of temperature arising from changes in barometric pressure, as their effect would evidently be entirely negligible.

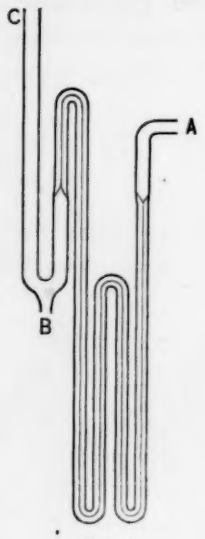

Fig. 1.

Any desired difference of pressure at the two ends of the capillary was attained by inserting a tube in the ground joint and connecting it with a large air reservoir *R*, which was itself connected through the cock *S* with a suction pump and with an open mercury manometer *M*. The gas or vapor entered at the other end of the capillary always under atmospheric pressure. The whole apparatus in the form used for measuring the rate of transpiration of the mercury vapor is shown in Fig. 2.

In making the experiments, the rate of flow of the mercury vapor was first determined in the following manner: While the cylinder was being heated, carbon dioxide was forced through the capillary to prevent the condensation in it of liquid mercury, and the formation of its oxide. After the mercury was boiling actively, and its vapor entirely enveloped the capillary, as shown by a mercurial thermometer inserted in the tube *B* (Fig. 2), it was connected

with the suction pump, and mercury vapor drawn through for half an hour. The carefully ground end of a weighed bulb *W* was then inserted in the ground joint, its other end being connected, by means of a clamped rubber tube *C*, with the air reservoir, in which the desired reduction of pressure had been produced. At a definite moment the clamp *C* was opened and the time noted. As the volume of the condensing bulb *W* was very small, compared

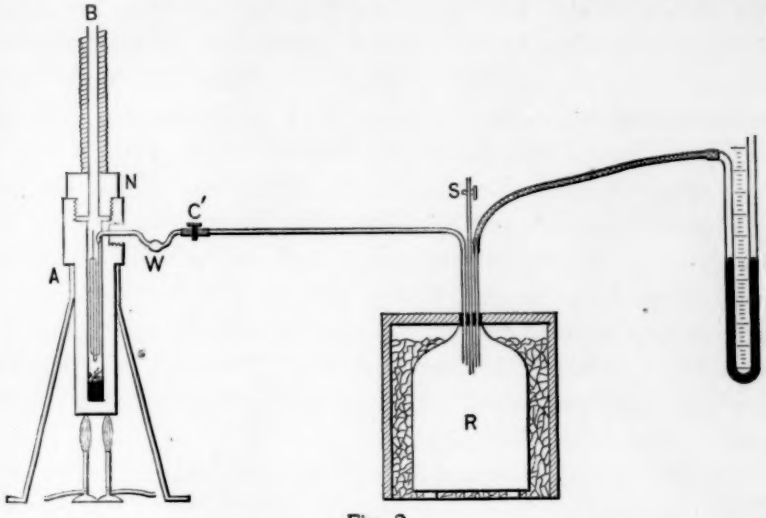

Fig. 2.

with the volume of the air reservoir, no sensible change in the pressure was thus produced. The mercury vapor was found to be completely condensed in *W* about two or three centimeters from the ground joint.

It was found that a slight and unavoidable leakage[1] through the ground joint occurred, and it was therefore necessary to readjust the pressure occasionally. It could easily be maintained constant to 0.2 or 0.3 mm., or even closer. After a sufficient time, usually sixty minutes, the clamp *C*[1] was closed, and at a noted instant the bulb removed and subsequently weighed. Check experiments were made in this way at each of two or three different pressures.

[1] In the case of the mercury experiments, no error could arise from this source, as the leakage was inward. In the case of those with carbon dioxide and hydrogen, it was proved by blank experiments that the amounts of carbon dioxide and water which leaked in were less than one per cent of the total weight.

The capillary was now removed from the cylinder, and the opening B (Fig. 1) carefully closed by fusion. A glass tube, long enough to project beyond the upper end of B (Fig. 2), was also fused on to the end C, and the capillary was then ready for the experiments with carbon dioxide and hydrogen. It was replaced in the cylinder as before, and the glass tube projecting through B connected through suitable wash-bottles with the gas generator. The carbon dioxide was made in a Kipp generator by the action of dilute sulphuric acid on lumps of pure fused sodium carbonate, and was dried by passing through two Allihn gas wash-bottles containing strong sulphuric acid. The hydrogen was prepared from pure Bertha zinc and dilute sulphuric acid, as in the case of the carbon dioxide, and was purified by means of caustic soda solution and concentrated sulphuric acid. In order to maintain the gas entering the capillary at atmospheric pressure, a T-tube was inserted between the wash-bottles and the capillary, and its perpendicular arm was turned downwards, and caused to dip into sulphuric acid barely below its surface. The cock of the generator was opened sufficiently to cause the gas to bubble out steadily through the sulphuric acid.

The transpiration measurements were made as in the case of the mercury. The carbon dioxide flowing through in a definite time was determined by absorption in weighed tubes filled with lumps of soda lime. The hydrogen was burned by passing it over hot copper oxide, contained in hard glass tubes, from which the air had been previously displaced by carbon dioxide, and the water formed was collected in weighed calcium chloride tubes.

The results are presented in the following table. In the first column is given the symbol of the substance; in the second, the atmospheric pressure p_1; in the third, the difference in pressure $(p_1 - p_2)$; in the fourth, the time t, expressed in hours; in the fifth, the weight w, in grams, of the substance weighed; in the sixth, the mean weight transpired in one hour as computed from the separate check experiments; and in the last, the quotient obtained by dividing this weight by the molecular weight m of the substance, the time, and the pressure function

Series I.

SMALLER CAPILLARY.

	p_1	$p_1 - p_2$	t	w	$w : t$	$\frac{w \times 10^{10}}{tm(p_1^2 - p_2^2)}$
Hg	753	200	1½	0.738	—	—
	753	—	1½	0.740	—	—
	756	—	1½	0.745	0.494	93.6
	755	300	1	0.685	—	—
	755	—	1	0.686	0.686	93.6
	754	400	1	0.834	—	—
	754	—	1	0.831	0.833	92.9
CO_2	752	200	1	0.237	—	—
	752	—	1	0.239	—	—
	752	—	1½	0.357	0.238	205.0
	759	300	1	0.329	—	—
	759	—	1	0.327	—	—
	766	—	1	0.324	0.327	203.0
	766	400	1	0.400	—	—
	766	—	1	0.396	—	—
	759	—	1	0.396	0.397	202.0

Series II.

LARGER CAPILLARY.

	p_1	$p_1 - p_2$	t	w	$w : t$	$\frac{w \times 10^{10}}{tm(p_1^2 - p_2^2)}$
Hg	769	150	1	1.548	—	—
	769	—	1	1.548	1.548	374
	769	300	1	2.763	—	—
	769	—	1	2.764	—	—
	769	—	1	2.739	2.755	373
CO_2	765	150	1	0.704	—	—
	765	—	1	0.706	0.705	774
	765	300	1	1.267	—	—
	765	—	1	1.264	1.265	779
H_2	766	150	1	0.557	—	—
	766	—	1	0.557	0.557	1517
	766	300	1	1.009	—	—
	766	—	1	1.006	1.008	1496
Hg	766	300	1	2.728	—	—
	766	—	1	2.746	—	—
	764	—	1	2.743	2.739	371

$(p_1^2 - p_2^2)$.[1] (See preceding expression (2), p. 3.) As the headings indicate, the first of these two series of experiments was made with the smaller and the second with the larger capillary. It will be seen that in the second series two sets of determinations are given for mercury vapor. The first one was made before, and the second one after, the experiments with carbon dioxide and hydrogen, and their agreement shows that the capillary had undergone no change by stoppage or otherwise during the course of the experiments with it.

Attention may be first called to the agreement of the values of the last column, in the case of the transpiration of the same substance under different differences of pressure, thus proving that the effect of pressure is in close accordance with that required by the formula, and consequently that the capillaries are of sufficient length and small enough bore to give the true values of the viscosity coefficients.

Of the two series of experiments the first one made with the smaller capillary is to be regarded as less reliable by reason of the fact that, owing to an accident to the capillary, check experiments with mercury vapor after completion of those with carbon dioxide could not be made as in the former case, in consequence of which it is not certain that a stoppage did not occur in the course of the series. While there was nothing to indicate that such was the case, yet, on account of its extremely small bore, it was much more liable to stoppage than the larger capillary. We consider the experiments with the latter to be certainly accurate within two per cent.

Nevertheless, the agreement between the results of the first and the second series is perhaps as close as could be expected with capillaries so different from each other in character. The relative viscosity coefficients of the different gases were calculated from the values of the last column in the table by means of formula (2). The results are as follows:

[1] In the calculation of this quantity, the same mean value of p_1 was used in all the experiments of each series; namely, 760 for those with the smaller capillary, 765 for those with the larger.

FIRST SERIES.

$$\frac{\eta_{Hg}}{\eta_{CO_2}} = 2.17.$$

SECOND SERIES.

$$\frac{\eta_{Hg}}{\eta_{CO_2}} = 2.08. \quad \frac{\eta_{Hg}}{\eta_{H_2}} = 4.04. \quad \frac{\eta_{CO_2}}{\eta_{H_2}} = 1.94.$$

The relative values for mercury and carbon dioxide agree within about four per cent. That of the second series is, however, more reliable, for the reason above stated, and will be used in the subsequent calculations. It may be noted that the value of the ratio $\eta_{CO_2} : \eta_{H_2}$ at ordinary temperature is 1.72,[1] somewhat smaller than that found by us at 357°, a result which is in accordance with the greater temperature coefficient of carbon dioxide established by several investigators.

The corresponding values of the relative mean cross-sections as calculated by formula (1) are

$$\frac{q_{Hg}}{q_{CO_2}} = 1.02\,; \quad \frac{q_{Hg}}{q_{H_2}} = 2.48.$$

That is to say, the average cross-section of the mercury molecule or atom is very nearly the same as that of the carbon dioxide molecule, and is about $2\frac{1}{2}$ times as large as that of the hydrogen molecule. This last result does not differ very greatly from that (2.68) corresponding to the relative molecular volumes of mercury and hydrogen as calculated for 300° by Koch.

These results indicate that *atoms and molecules are of the same order of magnitude*, and that the spaces between the atoms within the molecule, if any exist, are not large in comparison with those occupied by the atoms themselves. And, consequently, the viscosity of gases or any other property which, like it, is dependent only on the size or form of the molecules is not adapted for distinguishing between monatomic and polyatomic molecules.

In considering the significance of the above values of the cross-section, the different masses of the various molecules, to be sure,

[1] O. E. Meyer, Kinetische Theorie der Gase, 142.

ought not to be entirely disregarded. The mercury and carbon dioxide have, as we have seen, the same cross-section, and, therefore, assuming both to be of the same general form, they occupy the same volume. The mass of the former is, however, 4.55 times as great as that of the latter. The density of the mercury molecule is consequently greater in this same proportion. But this difference is not marked enough to make it necessary to attribute it to free space within the carbon dioxide molecule. For it is not improbable that the inherent density of massive atoms, like those of mercury, may be considerably greater than that of light atoms, like those of carbon and oxygen.

In closing we desire to point out that the principle here established that atoms and molecules are of the same order of magnitude, and that no considerable free interatomic spaces exist within the molecule, is in accordance with the remarkable fact that the molecular cross-section of most comparatively simple molecules is approximately an additive property calculable from certain constant values of the atomic cross-section.[1] This fact would be unintelligible were the principle not correct; for, if considerable space existed between the atoms, it is not to be supposed that those spaces would be the same in entirely dissimilar molecules — that, for example, the space between the hydrogen and chlorine atoms in hydrochloric acid would have any relation to the spaces between the atoms in the elementary gases hydrogen and chlorine.

[1] See O. E. Meyer, Kinetische Theorie der Gase, 209.

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MINOR CONTRIBUTIONS.

An Example in Thermometry.[1]

By A. S. Cole and E. L. Durgan.

SINCE the publication of the methods of procedure employed at the International Bureau of Weights and Measures, at Breteuil, the ordinary method of obtaining the corrections of a thermometer by comparison with another thermometer whose errors are known, is neither defensible on the score of precision nor on the score of economy in time. The determination of the absolute corrections of a thermometer at a large number of points requires but little more time than the determination of the relative corrections at a few points.

The details of the absolute method are scattered through three volumes of the *Memoirs* of the Bureau, and, being written in French, they are not readily available to the English student. The study of thermometer Gerhardt No. 2403 is given in the following paper as an illustration of the new method of procedure.

The observed reading of a thermometer is subject to the following corrections: —

(1) A correction for calibration.

(2) Corrections for external and internal pressure.

(3) A correction for the fundamental interval between the 0° point and the 100° point. These corrections will be considered in the order in which they are named.

The Calibration of a Thermometer.

We take, as an example, the calibration of the 10° points of thermometer Gerhardt No. 2403. If the graduations upon the stem are exactly equal in value, the corrections to these values will be indicated by the lengths of a column of mercury placed successively end to end for each of the 10° points. Since it is not easy to break off a column having a definite length, we must measure the excess of the length of the column over the length of the successive 10° graduations. If we designate the excess of the length of the column over the length of the 10° spaces by λ, we have only to apply to

[1] Contribution from the Shannon Physical Laboratory of Colby University.

each of the 10° graduations successively the values $\frac{\lambda}{10}, \frac{2\lambda}{10}, \cdots, \frac{10\lambda}{10}$, in order to obtain the corrected values of the 10° points of the thermometer.

But we cannot assume that all the subdivisions of the scale are equal. (1) Let $x_1, x_2, x_3, x_4, \cdots, x_{11}$ represent the *corrections* to the 10° points of the scale. Represent the observed excess of the length of the column by $a_1, a_2, a_3, a_4, \cdots, a_{10}$; then, for any space, *e.g.* between the line 0° and line 10°, the true relation will be expressed by the equation: —

$$x_1 - x_2 + \lambda = a_1.$$

Following the notation given on p. C 37, Vol. II., we shall have a series of equations of the form: —

(2)
$$\begin{aligned} x_1 - x_2 + \lambda_{10} &= a_1, \\ x_2 - x_3 + \lambda_{10} &= a_2, \\ \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \\ x_{10} - x_{11} + \lambda_{10} &= a_{10}. \end{aligned}$$

Breaking off successively columns having the lengths 10°, 20°, 30°, 40°, 50°, 60°, 70°, 80°, and 90°, and measuring the excess of these columns over the corresponding spaces, we have a series of fifty-four equations to be solved by the process of least squares.

It is to be noted that the signification of λ, which was assigned to it under the supposition of equal subdivisions of the entire length of the scale, does not hold when we assume that the divisions have the corrections x_1, x_2, x_3, x_4, etc. In this case, this constant will be affected by the assumption that the scale graduations themselves require corrections.

We take, as an example of calibration, thermometer Gerhardt No. 2403. The readings were all made with a telescope of short focus and a filar micrometer, in which one division equals 0°.00066. The method of making the observations will appear from the following example: —

Let R_l = the micrometer reading of the graduated scale, *e.g.* for 0°.
R_u = the micrometer reading of the upper end of the division, *e.g.* for 10°.
R_m = the micrometer reading of the miniscus of the mercury column.
n = the number of tenths of the graduations between which the miniscus falls.

By estimation.	Measurement with the micrometer.	
	For 0°.	For 10°.
l= 0.025	R_l= 82 div.	R_l= 44 div.
u=10.110	R_m=131 div.	R_m= 62 div.
$u-l$=10.085	R_u=261 div.	R_u=224 div.
	n=0.000	n=0.10 1 div.=0.00066
	$\frac{49}{179}\times 0.1=0.027$	$\frac{18}{180}\times 0.1=0.010$
	Sum=0.027	Sum=0.110
	0.110 − 0.027 = +0.083.	

All the measurements for this series of observations were made in the manner indicated above. We take as an example of the method of reducing the observations given in the first column of Table I.

Interval.	Observed reading.	Relative errors.	Relative corrections.
° °	°	°	°
0- 10	10.019	−0.001	+0.001
10- 20	10.034	+0.014	−0.014
20- 30	10.006	−0.014	+0.014
30- 40	10.030	+0.010	−0.010
40- 50	10.034	+0.014	−0.014
50- 60	10.008	−0.012	+0.012
60- 70	10.012	−0.008	+0.008
70- 80	10.020	+0.000	+0.000
80- 90	10.075	+0.055	−0.055
90-100	10.012	−0.008	+0.008
Mean	10.020		

At this point two courses are open to us. Either we may take the results obtained by subtracting 10 from each of the values, or we may obtain a set of residuals by subtracting the mean value of column (1) from each separate value giving column (2). In the former case we must follow formulæ 1 and 8 given on pp. 8 and 12, Vol. V. In the latter case, the values of s and Σ become zero, and the reduction becomes more simple. We shall in this example follow the latter method. [See a paper on the Cumulative Errors of a Graduated Scale, by W. A. Rogers, *Proceedings Mechanical Engineers*, Vol. XV. The correction is here noted that the denominations S given on p. 134 should be written in small type.]

The numerical data given in Table I. has been obtained from the mean of independent observations taken by each of us.

(3) TABLE I.

λ_{10}		λ_9		λ_8		λ_7		λ_6	
° °	°	° °	°	° °	°	° °	°	° °	°
0– 10	+0.001	0– 20	−0.027	0– 30	+0.014	0– 40	−0.001	0– 50	−0.022
10– 20	−0.014	10– 30	−0.005	10– 40	−0.016	10– 50	−0.055	10– 60	−0.036
20– 30	+0.014	20– 40	+0.003	20– 50	−0.038	20– 60	−0.035	20– 70	+0.004
30– 40	−0.010	30– 50	−0.039	30– 60	−0.040	30– 70	−0.004	30– 80	−0.001
40– 50	−0.014	40– 60	−0.012	40– 70	+0.016	40– 80	+0.025	40– 90	+0.014
50– 60	+0.012	50– 70	+0.048	50– 80	+0.035	50– 90	+0.037	50–100	+0.041
60– 70	+0.008	60– 80	+0.036	60– 90	+0.034	60–100	+0.043		
70– 80	+0.000	70– 90	−0.009	70–100	−0.005				
80– 90	−0.005	80–100	+0.005						
90–100	+0.008								

λ_5		λ_4		λ_3		λ_2	
0– 60	−0.038	0– 70	+0.017	0– 80	+0.014	0– 90	+0.002
10– 70	−0.002	10– 80	−0.012	10– 90	−0.018	10–100	−0.002
20– 80	+0.002	20– 90	+0.001	20–100	+0.004		
30– 90	+0.013	30–100	−0.006				
40–100	+0.025						

Since the coefficients of the unknown quantities are all unity, we have only to take the sums of the coefficients, in order to obtain the solution by least squares. Table II. is obtained by writing the figures in vertical columns, commencing at the left in the horizontal columns. The same figures are then written below the line of division with their signs changed. (See Table II. on following page.)

FORMULÆ FOR COMPUTING THE QUANTITIES D AND R.

$$D_{11} = t_{11} - t_1 \qquad R_{10} = \tfrac{1}{11}(D_{10} - D_{11})$$
$$D_{10} = t_{10} - t_2 \qquad R_9 = \tfrac{1}{11}(D_9 - D_{10})$$
$$D_9 = t_9 - t_3 \qquad R_8 = \tfrac{1}{11}(D_8 - D_5)$$
$$D_8 = t_8 - t_4 \qquad R_7 = \tfrac{1}{11}(D_7 - D_8)$$
$$D_7 = t_7 - t_5$$

CALCULATION OF D AND R.

$t_{11} = -0.113$	$t_{10} = -0.061$	$t_9 = -0.027$	$t_8 = -0.101$	$t_7 = +0.198$
$-t_1 = +0.040$	$-t_2 = +0.151$	$-t_3 = +0.004$	$-t_4 = +0.120$	$-t_5 = -0.078$
$D_{11} = -0.073$	$D_{10} = +0.090$	$D_9 = -0.023$	$D_8 = +0.019$	$D_7 = +0.120$
	$-D_{11} = +0.073$	$-D_{10} = -0.090$	$-D_9 = +0.023$	$-D_8 = -0.019$
	$11\,R_{10} = +0.163$	$11\,R_9 = -0.113$	$11\,R_8 = +0.042$	$11\,R_7 = +0.001$
	$R_{10} = +0.014$	$R_9 = -0.010$	$R_8 = +0.004$	$R_7 = +0.000$

FORMULÆ FOR THE COMPUTATION OF THE QUANTITY Q.

$$Q_{10} = R_{10} + Q_{11} - \frac{2}{10} Q_{11} \qquad Q_8 = R_8 + Q_9 - \frac{2}{3 \times 8}(Q_{11} + Q_{10} + Q_9)$$

$$Q_9 = R_9 + Q_{10} - \frac{2}{2 \times 9}(Q_{11} + Q_{10}) \qquad Q_7 = R_{77} + Q_8 - \frac{2}{4 \times 7}(Q_{11} + Q_{10} + Q_9 + Q_8) \qquad Q_{11} = 0$$

TABLE II.

COMPUTATION OF $t_1, t_2, t_3, \cdots, t_{11}$.

x_1	x_2	x_3	x_4	x_5	x_6	x_7	x_8	x_9	x_{10}	x_{11}
+0.001	−0.014	+0.014	−0.010	−0.014	+0.012	+0.008	+0.000	−0.005	+0.008	
−0.027	+0.005	+0.003	−0.039	−0.012	+0.048	−0.036	−0.009	+0.005	−0.002	+0.002
+0.014	−0.016	−0.038	−0.040	+0.016	+0.035	+0.034	−0.005	−0.014	+0.018	−0.004
−0.001	−0.055	−0.035	−0.004	+0.025	+0.037	+0.034	−0.017	+0.012	−0.001	+0.006
−0.022	−0.036	+0.004	−0.001	+0.014	+0.014	+0.038	+0.002	−0.002	−0.013	−0.025
−0.038	−0.002	+0.002	+0.013	+0.025	+0.022	+0.036	−0.004	+0.001	−0.014	−0.041
+0.017	−0.012	+0.001	−0.006	+0.001	+0.055	+0.035	+0.004	−0.025	−0.037	−0.043
+0.014	−0.018	+0.004	−0.014	+0.016	+0.038	+0.040	−0.016	−0.035	−0.043	+0.005
+0.002	−0.002	+0.027	−0.005	−0.003	+0.039	+0.012	−0.048	+0.036	+0.009	−0.005
	−0.001	+0.014	−0.014	+0.010	+0.014	−0.012	−0.008	−0.000	+0.005	−0.008
−0.010	−0.151	−0.004	−0.120	+0.078	+0.341	+0.198	−0.101	−0.027	−0.061	−0.113
t_1	t_2	t_3	t_4	t_5	t_6	t_7	t_8	t_9	t_{10}	t_{11}

CHECK.

$$t_1 \quad t_2 \quad t_3 \quad t_4 \quad t_5 \quad t_6 \quad t_7 \quad t_8 \quad t_9 \quad t_{10} \quad t_{11} = 0.$$
$$-0.040 - 0.151 - 0.004 - 0.122 + 0.073 + 0.311 + 0.198 - 0.101 - 0.027 - 0.061 - 0.113 = 0.$$

FORMULÆ FOR THE COMPUTATION OF THE QUANTITY *P*.

$S_{11} = t_{11} + t_1$ $\quad$ $11\,P_{11} = S_{11} + 2X$ $\quad$ $11\,P_{11} = 0$

$S_{10} = t_{10} + t_2$ $\quad$ $11\,P_{10} = S_{10} + 2X$ $\quad$ Since $P_{11} = X_{11} + X_1$

$S_9 = t_9 + t_3$ $\quad$ $11\,P_9 = S_9 + 2X$ $\quad$ $\therefore 2X = -S_{11}$

$S_8 = t_8 + t_4$ $\quad$ $11\,P_8 = S_8 + 2X$

$S_7 = t_7 + t_5$ $\quad$ $11\,P_7 = S_7 + 2X$

$S_6 = t_6 + t_6$ $\quad$ $11\,P_6 = S_6 + 2X$

CALCULATION OF *S* AND *P*.

$t_{11} = -0.113$	$t_{10} = -0.060$	$t_9 = -0.027$	$t_8 = -0.101$	$t_7 = +0.198$	$t_6 = +0.341$
$t_1 = -0.040$	$t_2 = -0.151$	$t_3 = -0.004$	$t_4 = -0.120$	$t_5 = +0.078$	$t_6 = +0.341$
$S_{11} = -0.153$	$S_{10} = -0.212$	$S_9 = -0.031$	$S_8 = -0.221$	$S_7 = +0.276$	$S_6 = +0.682$
$2X = +0.153$	$2X = +0.153$	$2X = +0.153$	$2X = +0.153$	$2X = +0.153$	$2X = +0.153$
$11\,P_{11} = 0$	$11\,P_{10} = -0.059$	$11\,P_9 = +0.122$	$11\,P_8 = -0.068$	$11\,P_7 = +0.429$	$11\,P_6 = +0.835$
$P_{11} = 0$	$P_{10} = -0.005$	$P_9 = +0.011$	$P_8 = -0.006$	$P_7 = +0.039$	$P_6 = +0.076$

CHECK.

$P_{11} + P_{10} + P_9 + P_8 + P_7 + \frac{1}{2}P_6 = x.$

$0 - 0.005 + 0.011 - 0.006 + 0.039 + 0.038 = +0.077.$

CALCULATION OF Q.

$Q+R-\frac{1}{p}\Sigma Q$	ΣQ	p	$\frac{1}{p}\Sigma Q$
$Q_{11} =$ + 0.000		5	
$Q_{10} =$ + 0.014	+0.014	9	−0.002
$Q_9 = -0.010 + 0.014 + 0.002 = +0.006$	+0.020	12	+0.002
$Q_8 = +0.004 + 0.003 - 0.002 = +0.007$	+0.027	14	+0.002
$Q_7 = +0.000 + 0.006 - 0.002 = +0.004$	+0.031		

FORMULÆ FOR COMPUTING $x_1, x_2, x_3, \cdots, x_{11}$.

$$x_{11} = \tfrac{1}{2}(P_{11} + Q_{11}) \qquad x_1 = \tfrac{1}{2}(P_{11} - Q_{11})$$
$$x_{10} = \tfrac{1}{2}(P_{10} + Q_{10}) \qquad x_2 = \tfrac{1}{2}(P_{10} - Q_{10})$$
$$x_9 = \tfrac{1}{2}(P_9 + Q_9) \qquad x_3 = \tfrac{1}{2}(P_9 - Q_9)$$
$$x_8 = \tfrac{1}{2}(P_8 + Q_8) \qquad x_4 = \tfrac{1}{2}(P_8 - Q_8)$$
$$x_7 = \tfrac{1}{2}(P_7 + Q_7) \qquad x_5 = \tfrac{1}{2}(P_7 - Q_7)$$
$$x_6 = \tfrac{1}{2}P_6$$

CALCULATION OF $x_1, x_2, x_3, \cdots, x_{11}$.

Indices.	P	Q	$P+Q$	$P-Q$		
11	+0.000	+0.000	+0.000	+0.000	$x_{11} =$ 0.0	$x_1 =$ 0.0
10	−0.005	+0.014	+0.009	−0.019	$x_{10} = +0.005$	$x_2 = -0.010$
9	+0.011	+0.006	+0.017	+0.005	$x_9 = +0.009$	$x_3 = +0.002$
8	−0.006	+0.007	+0.001	−0.013	$x_8 = +0.001$	$x_4 = -0.007$
7	+0.039	+0.004	+0.043	+0.035	$x_7 = +0.021$	$x_5 = +0.018$
6	+0.076		+0.076		$x_6 = +0.038$	

CHECK.

Sum of $x1 + x2 + x3 + x4 + x5 + x6 + x7 + x8 + x9 + x10 + x11 = -\frac{1}{2}S_{11}$.

0.000−0.010+0.002−0.007+0.018+0.038+0.021+0.001+0.009+0.005+0.000 = +0.077.

FORMULÆ FOR THE COMPUTATION OF $\lambda_2 \cdots \lambda_{10}$.

$$2\lambda_2 = S_2 + Q_{11} + Q_{10} \qquad \lambda_2 = +0.007$$
$$3\lambda_3 = S_3 + Q_{11} + Q_{10} + Q_9 \qquad \lambda_3 = +0.006$$
$$4\lambda_4 = S_4 + Q_{11} + Q_{10} + Q_9 + Q_8 \qquad \lambda_4 = +0.007$$
$$5\lambda_5 = S_5 + Q_{11} + Q_{10} + Q_9 + Q_8 + Q_7 \qquad \lambda_5 = +0.006$$
$$6\lambda_6 = S_6 + Q_{11} + Q_{10} + Q_9 + Q_8 + Q_7 \qquad \lambda_6 = +0.005$$
$$7\lambda_7 = S_7 + Q_{11} + Q_{10} + Q_9 + Q_8 \qquad \lambda_7 = +0.004$$
$$8\lambda_8 = S_8 + Q_{11} + Q_{10} + Q_9 \qquad \lambda_8 = +0.003$$
$$9\lambda_9 = S_9 + Q_{11} + Q_{10} \qquad \lambda_9 = +0.002$$
$$10\lambda_{10} = S_{10} + Q_{11} \qquad \lambda_{10} = +0.000$$

Substituting in the original equations,

$$x_1 - x_2 + \lambda_{10} = a_1, \quad x_1 - x_3 + \lambda_9 = b_1, \quad x_1 - x_4 + \lambda_8 = c_1, \text{ etc.},$$

we have

CALCULATION OF RESIDUALS.

+0.009	+0.027	−0.004	−0.013	−0.011	−0.015	−0.011	−0.017	+0.000
+0.002	+0.004	−0.009	+0.011	+0.010	−0.003	+0.000	+0.009	−0.001
−0.005	−0.017	+0.004	+0.020	+0.002	−0.003	+0.003	+0.004	
+0.015	−0.004	+0.015	+0.000	−0.010	−0.019	+0.006		
−0.006	+0.011	+0.003	−0.012	+0.004	−0.001			
+0.005	−0.009	−0.003	+0.000	+0.002				
+0.012	−0.002	−0.015	−0.018					
−0.008	+0.007	+0.009						
+0.009	+0.006							
−0.003								

As a check upon the values of the corrections thus obtained, it may be found profitable to compare these results with those found by the method in use at the Shannon Physical Laboratory of Colby University.

This method consists in the *independent* measurement of the corrections for the scale divisions and of the equal-volume points of the mercurial column for any selected length.

It is obvious that the final corrections will be found by subtracting the equal-scale corrections from the equal-volume corrections for the same points, since the graduations upon the scale must correspond in position with the position of equal-volume points.

This method seems to possess three distinct advantages.

(1) In the ordinary method only a low magnifying power can be used in the telescope or the microscope employed, on account of the necessity of observing the scale and the column at the same time. In this method each focus is obtained independently.

(2) It can only be assumed that the equal-volume points hold true for the middle point of the column. This method allows the zero point of the scale corrections to be coincident with the zero of the equal-volume corrections.

(3) Since the value of the equal volume corrections will, in a good thermometer, have a considerable degree of symmetry, it will be possible to obtain a smooth curve for single degrees from observation at a few points. Since the operation of obtaining the corrections of the single degree points of the scale involves but slight labor, it will be found feasible to obtain the calibration corrections for a large number of points by taking the corrections for the equal-volume points from the constructed curve.

These advantages will be more clearly seen in the example given below.

The data are taken by the stop method. The stops of the comparator are set a distance apart equal approximately to the length of the spaces to be compared. The microscope carriage having been brought into contact with the stop on the left, the micrometer of the microscope is brought into coincidence with, *e.g.*, the line for 0°. The carriage is then brought into contact with the stop on the right and the reading for the coincidence with line 5° is taken. The difference in these readings will give the deviation from the distance between the stops expressed in divisions of the micrometer. In the same way the deviation of the remaining spaces from the constant distance between the stops will be obtained. Column 1 of Table III. contains the values derived from the observation in the manner described. Column 2 of this table contains the results obtained after subtracting the mean of the values in the first column from each value of the screw, since in this method, an increasing reading of the micrometer screw indicates that the space measured is too short. We thus obtain the relative corrections with respect to the mean value of the corrections. The values in column 3 are obtained by the summation of the values in column 2. These values represent the derived corrections which are to be applied to the actual divisions of the scale in order to obtain the subdivision of the total length of the scale into equal parts.

In the same way the corrections for the equal volume points of the corresponding points of the tube are obtained.

It is to be noted that when this method of discussion is applied to the measured excess of the mercury column over the distance selected between the scale divisions, we shall obtain *exactly* the same results as are derived from the same data by the more complex formulæ in the method of Kohlrausch.

The next column of this table contains the determined corrections to the scale readings for the 5° points. It will be seen that these values show a close agreement with the values derived by the method of Marek which are given in the column next following.

Thus far we have assumed that the equal volume corrections hold true for every part of the space occupied by the mercurial column in each of the 10° subdivisions. It is doubtful whether any reliable evidence upon this point can be derived from an examination of these observations, but the following method of investigation may throw a little light upon the subject. In Fig. 1 the two sets of corrections are laid off as ordinates, with the value of one small square for two units in the third decimal place. The equal-space corrections are represented by the full line curve, and the equal-volume corrections by the dotted curve. The values from which the curves are derived, are taken from Table I.

TABLE III.

	Scale divisions.	Relative corrections	Summed series = Σ.	Column calibrations	Relative corrections.	Summed series = Σ.	Final corrections.	By method of Marek.	Zero of Scale at 5°.		
									From computation.	From observation.	Mean.
°	°	°	°	°	°	°	°	°	°	°	°
									−0.029	−0.019	−0.024
0– 5	5.058	+0.028	+0.028	5.076	+0.036	+0.036	+0.008		+0.000	+0.000	+0.000
5– 10	5.057	+0.027	+0.055	5.057	+0.017	+0.053	−0.002	−0.010	+0.028	+0.019	+0.024
10– 15	5.054	+0.024	+0.079	5.065	+0.025	+0.078	−0.001		+0.054	+0.042	+0.048
15– 20	5.061	+0.031	+0.110	5.080	+0.040	+0.118	+0.008	+0.002	+0.086	+0.073	+0.079
20– 25	5.044	+0.014	+0.124	5.061	+0.021	+0.139	+0.015		+0.102	+0.092	+0.097
25– 30	5.041	+0.011	+0.135	5.036	−0.004	+0.135	+0.000	−0.007	+0.114	+0.108	+0.111
30– 35	5.014	−0.016	+0.119	5.017	−0.023	+0.112	−0.007		+0.100	+0.103	+0.102
35– 40	5.024	−0.006	+0.113	5.063	+0.023	+0.135	+0.022	+0.018	+0.096	+0.098	+0.097
40– 45	5.007	−0.023	+0.090	5.017	−0.023	+0.112	+0.022		+0.074	+0.089	+0.081
45– 50	5.016	−0.014	+0.076	5.054	+0.014	+0.126	+0.050	+0.038	+0.061	+0.072	+0.066
50– 55	5.014	−0.016	+0.060	5.038	−0.002	+0.124	+0.064		+0.047	+0.059	+0.053
55– 60	5.023	−0.007	+0.053	5.013	−0.027	+0.097	+0.044	+0.021	+0.041	+0.042	+0.041
60– 65	5.017	−0.013	+0.040	5.019	−0.021	+0.076	+0.036		+0.030	+0.033	+0.032
65– 70	5.015	−0.015	+0.025	5.093	−0.047	+0.029	+0.004	+0.001	+0.016	+0.023	+0.019
70– 75	5.012	−0.018	+0.007	5.027	−0.013	+0.016	+0.009		+0.000	+0.012	+0.006
75– 80	5.024	−0.006	+0.001	5.033	−0.007	+0.009	+0.008	+0.009	+0.006	+0.008	+0.001
80– 85	5.044	+0.014	+0.015	5.049	+0.009	+0.018	+0.003		+0.011	+0.013	+0.012
85– 90	5.040	+0.010	+0.025	5.061	+0.021	+0.039	+0.014	+0.005	+0.022	+0.015	+0.018
90– 95	5.019	−0.011	+0.014	5.015	−0.025	+0.014	+0.000		+0.013	+0.011	+0.012
95–100	5.016	−0.014	+0.000	5.026	−0.014	+0.000	+0.000	+0.000	+0.000	+0.000	+0.000
Mean . .	5.030		Mean . .	5.040							

In Fig. 2 the equal-volume curve is laid off for the midway points of the 5° subdivisions.

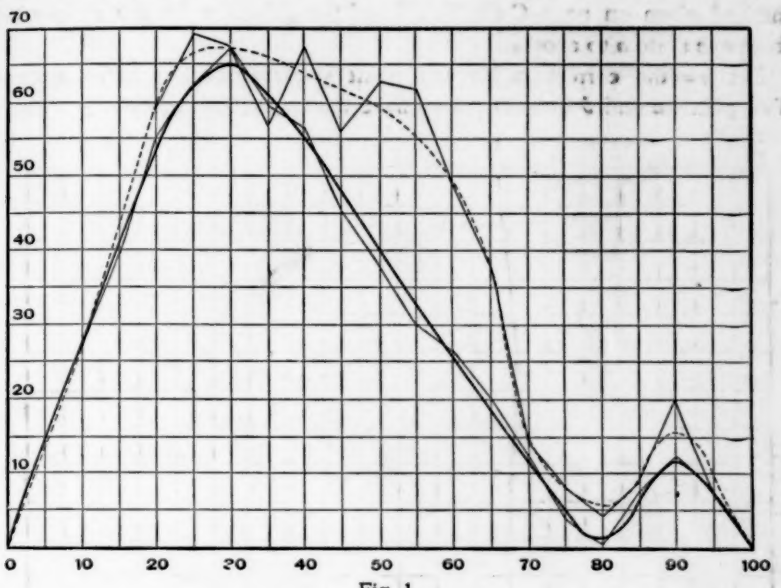


Fig. 1.

In Fig. 3 the zero of the equal space curve is taken at 5°. There are two methods of obtaining the data for this comparison. First, we can

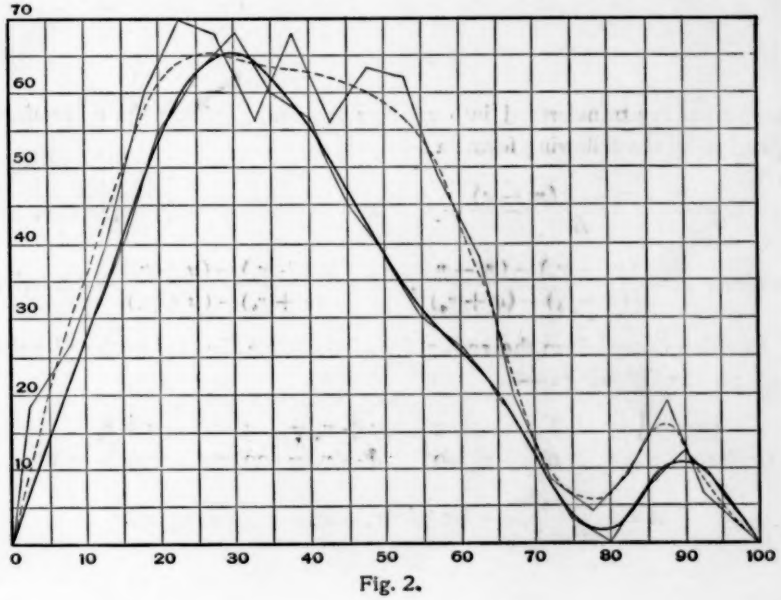


Fig. 2.

start the observed measures from this point, obtaining the results given in the last column but one of Table III. Secondly, we may employ the method given on page C 68, Vol. I., of the *Memoirs* for the conversion from one system to another.

Let $x =$ the correction for any point whatever in any given system. Two points a and b in this system have the corrections x_a and x_b. These

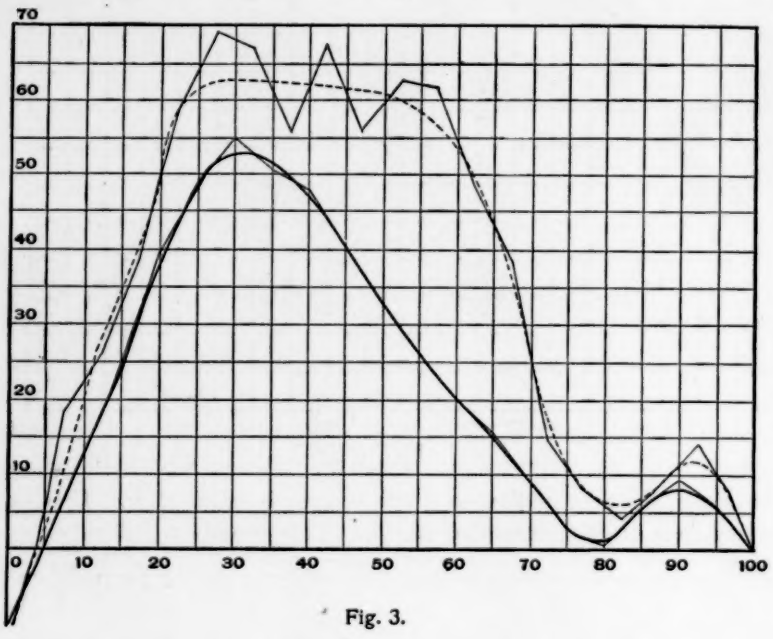


Fig. 3.

corrections are transformed into another system y_m, giving the corrections y_a and y_b by the following formula: —

$$(4)\quad y_m = \frac{x_n - x_a - A(m-a)}{B} + y_a = x_n - x_a - A(m-a) + y_n \text{ nearly,}$$

in which $A = \dfrac{(x_b - x_a) - (y_b - y_a)}{(b + y_b) - (a + y_a)}$, $\quad B = \dfrac{(b + x_b) - (a + x_a)}{(b + y_b) - (a + y_b)} = 1$ nearly.

In order to transform the zero point of the scale division to the 5° point we have the following: —

$a = 5$	$x_a = +28$	$y_a = 0$	$a + x_a = 5.028$	$a + y_a = 5.00$
$b = 100$	$x_b = 0$	$y_b = 0$	$b + x_b = 100.000$	$b + y_b = 100.00$

$$A = \frac{-0.028}{100 - 5} = -0.030 \qquad y_n = x_n - x_m + 0.030\, x_m.$$

For $n = 70°$ $y_n = +110 - 0.028 + 15 \times 0.030 = +0.086.$
For $m = 0°$ $y_n = 0 - 0.028 - 0.001 = 0.029.$
For $x_n = 60°$ $y_n = +55 - 0.028 + 55 \times 0.030 = +0.041.$

In this manner the values in the second column from the last of Table III. were computed, and the means of the computed and the observed values are given in the last column. The mean values thus obtained were used in laying off the equal space-curve in Fig. 3. The measured differences between the two curves in this figure will give the corrections given in Table I.

As far as these observations indicate, the values in column I. are a little nearer the correct values than those given in columns II. and III., since the sum of the squares of the vertical column for I. is less than from either II. or III.

Internal and External Pressure.

We now take up the corrections due to external and internal pressure upon the mercury in the bulb of a thermometer.

(5) Let d = the density of the water in which a thermometer is supposed to be immersed to a depth, below the surface, a distance h.
u = the distance of the middle point of the bulb to the zero point of the scale.
u_1 = the length of one degree expressed in millimeters.
δ_0 = the density of mercury at 0° C.
B = the observed reading of the barometer.
B' = the value of B reduced to 760 mm. at the level of the sea and at the latitude of 45°, by the formula

$$B' = B\frac{1 + 0.0000081\ T}{1 + 0.0001815\ T} \times \frac{g\phi}{g_{45°}},$$

in which the values of $\frac{g\phi}{g_{45°}}$, taken from the following table, are to be substituted.

ϕ	$\frac{g\phi}{g_{45°}}$	ϕ	$\frac{g\phi}{g_{45°}}$	ϕ	$\frac{g\phi}{g_{45°}}$
35°	0.99912	41°	0.99964	47°	1.00018
36	0.99921	42	0.99972	48	1.00027
37	0.99929	43	0.99982	49	1.00030
38	0.99937	44	0.99981	50	1.00045
39	0.99946	45	1.00000	51	1.00054
40	0.99955	46	1.00009		

TABLE IV.

CORRECTION TO 2403 FROM DIFFERENT CURVES.

	I.	II.	III.	Mean $= m_1$.	B = Marek.	$\frac{B+m^1}{2} = m_2$.	$m_2 - \text{I} = v_1$.	$m_2 - \text{II} = v_2$.	$m_2 - \text{III} = v_3$.	v_1^2	v_2^2	v_3^2
0	+ 0	− 3	+00	− 1	+ 0	+ 0	+ 0	+ 0	+ 0	0	0	0
5	+ 0	+ 6	+10	+ 5								
10	+ 2	+12	+20	+11	−10	+ 0	− 2	−12	−20	4	144	400
15	+ 2	+16	+20	+14								
20	+ 6	+20	+10	+15	+ 2	+ 8	+ 2	−12	−12	4	144	144
25	+ 9	+24	+ 5	+13								
30	+ 4	+18	− 2	+ 7	− 7	+ 0	− 4	−18	+ 2	16	324	4
35	+ 9	+22	+ 3	+11								
40	+16	+29	+14	+20	+18	+19	+ 3	−10	+ 5	9	100	25
45	+25	+38	+26	+31								
50	+30	+48	+35	+40	+38	+39	+ 1	− 9	+ 4	1	81	16
55	+44	+54	+38	+45								
60	+43	+54	+34	+44	+21	+32	−11	−22	− 2	121	484	4
65	+37	+50	+19	+38								
70	+13	+34	+ 4	+17	+ 1	+10	− 3	−24	+ 6	9	576	36
75	+ 5	+14	+ 4	+ 8								
80	+ 7	+10	+11	+ 9	+ 9	+ 9	+ 2	− 1	− 2	4	1	4
85	+ 6	+ 3	+10	+ 6								
90	+12	+ 6	+ 1	+ 6	+ 5	+ 5	− 7	− 1	+ 4	49	1	16
95	+ 5	+10	+ 2	+ 6								
100	+00	+00	+00	+00	+00	+ 0	+ 0	+ 0	+ 0	0	0	0
Sums										217	1855	649

Let P_e = exterior pressure for a vertical position.

P_i = interior pressure for a vertical position.

β_e = the coefficient of exterior pressure = a quantity whose reading increases in proportion to an increase of 1 mm. in the exterior pressure.

β_i = the coefficient of interior pressure = a quantity that diminishes in proportion as the interior increases 1 mm.

Designating the exterior pressure by γ_1, the interior pressure by γ_2, and their sum by γ, we have

$$\gamma = \beta_i(u + nu_1) - \beta_e(B' + \frac{h}{13.6} - 760).$$

The plate upon which is represented the apparatus for comparing thermometers, as shown facing page 237, will indicate the method of obtaining the value of β_e with a very brief explanation. The bulb of a thermometer is immersed in a bottle of water with an air-tight connection. The air space at the top of the bottle is connected with an air pump by means of a small lead pipe, a branch of this pipe being connected with a glass tube which is immersed in a reservoir of mercury, which serves as a manometer. The operation of obtaining the value of β_e is as follows: The thermometer is first read under atmospheric pressure. The air is then pumped from the bottle till the column in the manometer remains at a stationary height, when the height of the column is read in millimeters, and a second reading of the thermometer is taken. We have thus an observed difference in the height of the mercurial column corresponding to an observed difference in pressure. Or: —

$$(P_1 - P_0)\beta_e = t_1 - t_2,$$

$$\beta_e = \frac{t_1 - t_2}{P_1 - P_0}.$$

Care must be taken in these observations to allow considerable time to elapse after a change of pressure takes place, in order for the glass to take its normal condition under strain, otherwise much too large values of β_e will be obtained. As much as ten minutes should be allowed for this purpose. The mean of a sufficient number of observations gave for this thermometer

$$647\,\beta_e = 0.033°.$$

$$\therefore \quad \beta_e = 0.00005.$$

The value of the coefficient β_i is found by taking the difference between successive readings of a thermometer first in a vertical and then in a horizontal position.

All the observations which have been made at Breteuil agree in giving substantially the same value for β_i as for β_e for the same thermometer.

Since the coefficients for exterior and interior pressure are identical, the expression for the corrections can be simplified, giving, for a vertical point, —

$$(760 - B')\beta = \gamma_1,$$
$$(u + nu_1)\beta = \gamma_2.$$

The Fundamental Interval of a Thermometer.

If the reading of a thermometer in melting ice, when corrected for calibration error and for external and internal pressure, is zero, and if the reading in steam, at 760 mm. pressure, is exactly 100°, it is obvious that no correction for fundamental interval will be required. If under these conditions the thermometer, immersed in steam, at normal pressure, reads, *e.g.*, 100°.20, and the thermometer reads 0°.05 in melting ice, the difference between the two corrected values will give a quantity which is designated the fundamental interval of a thermometer. This difference must be distributed over the entire length of the distance between 0° and 100°. The chief difficulty in determining the true reading of a thermometer immersed in steam is the separate determination of the pressure of the steam. This is accomplished by means of a water barometer, as seen in the Regnault apparatus shown in Plate I. The method of procedure at Breteuil is as follows : —

Suppose that the reading of the barometer is 745.90 mm., that the reading of the water barometer is 12.7 mm. = 0.93 mm. for mercury, that the corrected reading of the zero point is — 0.363, and the corrected reading for steam 99°.369.

We first find the temperature corresponding to the pressure 745.90 + 0.93 = 746.83 mm. from the table following : —

Pressure.	T	Δ	Pressure.	T	Δ
mm.	°		mm.	°	
740	99.2577		750	99.6310	
		0.0376			0.0371
741	99.2953		751	99.6681	
		0.0374			0.0370
742	99.3321		752	99.7051	
		0.0375			0.0370
743	99.3702		753	99.7421	
		0.0373			0.0370
744	99.4075		754	99.7791	
		0.0374			0.0369
745	99.4449		755	99.8160	
		0.0373			0.0369
746	99.4822		756	99.8529	
		0.0372			0.0368
747	99.5194		757	99.8897	
		0.0373			0.0368
748	99.5567		758	99.9265	
		0.0371			0.0368
749	99.5938		759	99.9633	
		0.0372			0.0367
750	99.6310		760	1.0000	

Pressure.	T	Δ	Pressure.	T	Δ
mm.	°		mm.	°	
760	100.0000	0.0367	770	100.3649	0.0363
761	100.0367	0.0366	771	100.4012	0.0362
762	100.0733	0.0366	772	100.4374	0.0362
763	100.1099	0.0366	773	100.4736	0.0362
764	100.1465	0.0365	774	100.5098	0.0361
765	100.1830	0.0364	775	100.5559	0.0361
766	100.2194	0.0365	776	100.5820	0.0360
767	100.2559	0.0364	777	100.6180	0.0360
768	100.2923	0.0363	778	100.6540	0.0360
769	100.3286	0.0363	779	100.6900	0.0359
770	100.3649		780	100.7259	

From this table we find the temperature corresponding to 746.83 mm. = 99°.512.

True value $$1° = \frac{99.512}{99.369 - (-363)} - 1 = -0.00221.$$

Or, we may proceed as follows: —

Corrected 100° reading	= 99°.3690
Correction for pressure $= \frac{12.7 \times 0.0371}{13.6}$	= − 0.0345
Reading for pressure of 760 mm.	= 99°.3345
Reduction from 745 to 760 mm. $= 14.1 \times 0.0371$	= + 0.5231
True reading at 100°	= 99°.8576
True reading at 0°	= − 0.3630
Fundamental interval	= 100°.2206
Corrected $1° = \kappa$	= − 0.00221

There is one reason which seems to have considerable weight in favor of the latter method of reduction. If the reduced readings of the water barometer are subtracted from the observed temperature readings, the differences should be constant if the water barometer indicates the real steam pressure. It is just here that the observer is liable to serious error. It will be seen from the following example that the true reading of the barometer is obtained only after there has been a continuous constant steam pressure for at least twenty minutes. In the observations which follow it has been the practice to allow the thermometer to remain under a little greater than the normal pressure for about fifteen minutes, and after that under a constant pressure for about fifteen minutes longer.

The following is an example: —

OBSERVATION JANUARY 22, 1896.

T	Water manometer.	t	Δt	True t.
h. m.	mm.	°		°
9 25	3	100.218	−0.008	100.210
9 28	2	100.235	−0.005	100.230
9 30	7	100.292	−0.019	100.273
9 32	8	100.302	−0.021	100.281
9 36	9	100.320	−0.024	100.296
9 38	9	100.334	−0.024	100.310
9 42	9	100.327	−0.024	100.303
9 44	8	100.337	−0.024	100.313
9 46	9	100.348	−0.024	100.324
9 48	9	100.348	−0.024	100.324
9 52	5	100.340	−0.014	100.326

Following the practice at Breteuil, the reading for the zero point has been obtained from exposure to melting ice immediately *after* the exposure to steam. For this particular thermometer the time required for recovery from the depression of the zero point is about five hours, hence in the present instance it would make little difference whether the reading before or after exposure was selected. The latter reading has been selected on the score of uniformity of practice. These observations apparently furnish an additional reason for this choice, although additional observations at low pressures are needed to confirm the apparent fact that for low pressures all the thermometers investigated by Dr. Rogers have their readings lowered at the zero point, while no such effect is seen when the reading for the zero point is taken immediately after exposure to steam. It will be seen by an examination of the following table that the fundamental interval of this thermometer remains nearly constant.

Date.	B'	100°.		Depression.	t.
		Before.	After.		
	inches	°	°	°	°
Jan. 17	769.7	+0.000	−0.027	+ 0.027	100.110
Jan. 20, morning .	770.0	+0.004	−0.026	+ 0.030	100.108
Jan. 20, afternoon .	770.0	+0.006	−0.027	+ 0.033	100.166
Jan. 21, morning .	764.9	+0.003	−0.027	+ 0.030	100.122
Jan. 21, afternoon .	763.4	+0.004	−0.026	+ 0.030	100.147
Jan. 22, morning .	766.1	+0.007	−0.023	+ 0.030	100.152
Jan. 22, afternoon .	766.9	+0.000	−0.015	+ 0.015	100.138
Jan. 23, morning .	771.6	+0.011	−0.008	+ 0.019	100.169
Jan. 23, afternoon .	770.6	+0.000	−0.018	+ 0.018	100.152
Feb. 10, morning .	746.2	−0.070	+0.004	−[0.074]	100.129
Feb. 11, morning .	741.9	−0.107	−0.018	−[0.089]	100.135
Feb. 12, morning .	751.7	−0.003	−0.025	+ 0.022	100.166
Feb. 13, morning .	762.7	+0.006	−0.018	+ 0.024	100.150
Feb. 14, morning .	746.4	+0.004	−0.003	+ 0.007	100.152
Feb. 15, morning .	759.1	+0.011	+0.000	+ 0.011	100.136
Mean				+ 0.019	100.142

Determination of the Fundamental Interval by means of a Thermometer whose Fundamental Interval is known.

Let us suppose that a thermometer whose constants are fully determined is immersed to a depth h in water which has a nearly constant temperature. The temperature t will be determined by the equation

$$t = n + x_n + \gamma_1 + \gamma_2 - \zeta + \eta\kappa,$$

in which ζ = the reading for the corrected zero point $= n + x_n + \gamma_1 + \gamma_2$ for 0°, and $\eta = n_1 + x_n + \gamma_1 + \gamma_2$.

Very soon afterwards place in the liquid another thermometer whose constants are all known except ζ and κ. We shall then have, since the temperature of the liquid is supposed to remain constant,

$$t = [n_1 + x_2 + \gamma_1 + \gamma_2] = \zeta_x - n_1\kappa_x.$$

Immediately afterwards put this thermometer in melting ice and obtain a corrected reading for the zero point by the equation

$$t_0 = n_0 + x_n + \gamma_1 + \gamma_2 - \zeta_x.$$

Since for this point $\kappa_x = 0$, for the second thermometer we shall have

$$\zeta = (n_0 + x_n + \gamma_1 + \gamma_2)$$

$$\kappa_x = \frac{t}{(n_1 + x_n + \gamma_1 + \gamma_2) - \zeta}.$$

We take as an example the data for thermometer A given on p. D 11, Vol. I. It is required to find ζ and κ for thermometer G. The constants for these two thermometers are given on pp. D III. and D IV. For thermometer A we have

$$t = n + x_n + \gamma_1 + \gamma_2 - \zeta + \eta\kappa$$
$$13.025 + 0.1666 + 0.001 + 0.014 - 0.027 - 0.029 = 13.150.$$

For thermometer G we have

$$13.150 = 13.544 + 0.070 + 0.000 + 0.011 - \zeta = 13.626.$$

For t_0 we have

$$\zeta = n + x_n + \gamma_1 + \gamma_2$$
$$\zeta = +0.365 + 0.002 + 0.000 + 0.005 = +0.373,$$

then

$$\kappa = \frac{13.150}{13.626 - (+0.372)} - 1 = -0.00740,$$

$$\eta\kappa \text{ for } 13^\circ.6 = -0.101.$$

For a check we have

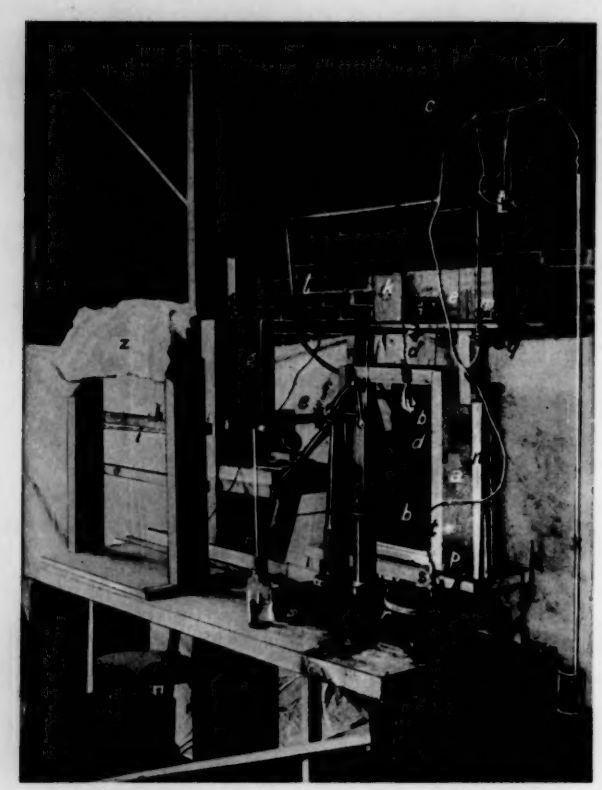
$$t = n_1 + x_n + \gamma_1 + \gamma_2 - \zeta + \eta\kappa$$
$$13^\circ.150 = 13.544 + 0.071 + 0.000 + 0.011 - 0.372 - 0.101 = 13^\circ.153.$$

We take as a second example the comparison of 2403, G. 2405, and Tounelot 62. The fundamental intervals for these thermometers are given below. Those for G. 2405 and T. 62 have been furnished by Dr. Rogers.

THE FUNDAMENTAL ELEMENTS.

	2403	2405	T. 62
	mm.	mm.	mm.
u = distance from center of bulb to zero of scale . . . . . =	69	60	63
n' = the number of degrees of any reading . . . . . =	...	...	...
u_1 = the value of one degree in millimeters . . . . . =	4.47	3.29	3.69
$n'u_1$ = the distance from zero of scale to an observed reading . . . . . =	$n' \times 4.47$	$n' \times 3.29$	$n' \times 3.69$
$u + n'u_1$ = distance of any reading from center of bulb . . . . . =	...	...	...
β = coefficient of external pressure . . =	0.00005	0.00016	0.00014
β_t = coefficient of internal pressure . . =	0.00005	0.00016	0.00014
ζ = corrected reading of zero point . . =	− 0.0016	− 0.001	+0.400
κ = constant derived from the fundamental interval. . . . . =	−0.00142	−0.00142	−0.0038

PLATE I.



Apparatus for the Comparison of Thermometers, and for Determining the Coefficient of External Pressure.

(a)(a') = water tank with windows of heavy plate glass in front and rear.
(b)(b') = paddle wheels driven by the pulley (c).
(k) = ice box.
(l) = connection with water pipe.
(m) = connection with steam pipe.
(q) = connection with water tank.
(g) = upright groove, in which the sliding block j is moved by a weight passing over a pulley.
(e) = telescope of very short focus.
(f) = filar micrometer.
(h) = frame upon which the thermometer (i) is mounted in a horizontal position.
(z) = sheet cotton for shading (i).
(d) = wire from which the thermometers are suspended in the water tank.
(n) = Regnault's steam comparing apparatus.
(o) = water barometer for measuring the excess over normal steam pressure.
(u)(s)(r)(x)(y) = apparatus for measuring the coefficient of external pressure.

DATA DERIVED FROM OBSERVATION.

(All the thermometers were immersed in water at a depth $h = 510$ mm. Observed barometer reading, 745.6 mm. Att. ther. = 8°.22. Reduced barometer = B' = 744.6 mm. 550 mm. for water = 38 mm. for mercury.)

	2403	2405	T. 62
	°	°	°
n . . . . . =	+6.727	+6.730	+6.259
x_n . . . . . =	+0.008	−0.002	−0.044
$\beta_e \times 15.4 = \gamma_1$ . . . . . =	+0.001	+0.002	+0.001
$-\beta_e \times 22\,6 = \gamma_1$ . . . . . =	−0.001	−0.003	−0.002
$\beta_i \times 10.19 = \gamma_2$ . . . . . =	+0.005	+0.013	+0.012
$-\zeta$. . . . . =	+0.016	+0.000	−0.461
n . . . . . =	+6.756	+6.740	+6.765
$\eta\kappa$ . . . . . =	−0.009	−0.008	−0.025
T . . . . . =	+6.747	+6.732	+6.740

In conclusion we desire to express our thanks to Dr. Rogers for assistance rendered in this investigation and for the use of the apparatus belonging to the Shannon Physical Laboratory of Colby University.

REFERENCES TO MEMOIRS OF THE INTERNATIONAL BUREAU.

Reference Nos.	I.	II.	V.
(1)	—	C 37	85
(2)	—	C 45	8
(3)	—	C 45–C 47	18–21
(4)	—	C 68	11
(5)	D 5–D 7	C 34	26–37
(6)	—	C 62	—
(7)	A 10–A 13	—	—
(8)	D 5	—	—
(9)	D 7	—	—
(10)	D 5	—	—
(11)	A 46–A 48	C 52–C 53	—
(12)	D 9–D 11	—	—
(13)	D 5–D 11	C 54–C 63	49–62
(14)	D 11	—	—
(15)	D 10–D 11	—	—
(16)	D 5	—	—

A STUDY OF THE APPARENT CAPACITY OF CONDENSERS FOR SHORT-CHARGE PERIODS.

BY HUBERT V. CARPENTER.

CONDENSERS have frequently been studied to find the quantity of electricity q contained in them after charging or discharging for varying lengths of time through very high resistances. Curves obtained from the results have been published,[1] and show the validity of the formula[2]

$$q = Q(e^{-\frac{t}{RC}}),$$

where q represents the quantity contained after discharging for a time t through a resistance R, and Q is the quantity corresponding to the theoretical capacity C for the given potential. Curves are also given[1] for different periods of charge through high resistance, which agree with the corresponding formula[2]

$$q = Q(1 - e^{-\frac{t}{RC}}).$$

This latter formula, verified by experiment, indicates that, with any value of R greater than zero, the quantity held by any condenser depends upon the time of charge, and that it increases toward the limit Q as the time increases. For any low value of R, however, the exponential term becomes negligible with extreme rapidity. Take, for example, the case in hand of condenser No. 1, with C equal to 10^{-6} farads and R about 0.4 ohm. Assume $t = 0.0001$ second and substitute in the formula

$$q = Q(1 - e^{-\frac{t}{RC}}) = Q(1 - 2.718^{-\frac{0.0001}{0.4 \times 10^{-6}}}) = Q[1 - 2.718^{-250}].$$

This shows that the exponential term may be safely neglected in experimental work, and that q is practically equal to Q.

There is, however, a difference in the apparent capacity of condensers that seems to depend upon the time of charge in much the same way as shown by the exponential term. This difference is overcome far too slowly, however, to be explained by the formula, and we must therefore look for some other cause. The usual explanation is, that the charge slowly "soaks into," or "is absorbed by," the dielectric; but just how or why this absorption takes place is hard to explain.

In order to determine the rate at which this soaking in takes place, and its amount for different types of condensers, the writer, in connection with Mr. E. W. Poole, undertook an experimental study of it. Three condensers were studied. Condenser No. 1 was a subdivided mica condenser,

[1] Nichol's Lab. Manual, Vol. II., p. 156.

[2] Bedell and Crehore's Alternating Currents, p. 72.

marked 1 microfarad, made by Queen & Co. No. 2 was a condenser, insulated with paraffined paper, constructed in the laboratory. No. 3 was made by the Stanley Electric Manufacturing Co., and has a very thin dielectric, whose composition is not stated. The resistance R in the charging circuit was made equal to 0.4 ohm. This low resistance was chosen in order to eliminate the effect of the exponential term in the formula for quantity.

In order to get data for very short charge periods, it became necessary to devise some method of charging which would allow accurate determinations of the time to be made. A method of doing this was suggested to us by Mr. B. E. Moore, who gave us many valuable suggestions throughout the work. This method consisted in the use of a Carhart pendulum interrupter[1] arranged to charge the condenser for a short period, and then discharge it instantly through a ballistic galvanometer having a long period of vibration. Corrections were made as shown in Fig. 1. The pendulum, swinging from left to right, overturns first the detent of K_1 and thus connects the battery to the condenser. When key K_2 is released, the battery circuit is broken, and the condenser is at once discharged through the galvanometer. Key K_2 was placed at the lowest point of the arc described by the pendulum, and key K_1 was moved along the arc to the left of K_2. The horizontal distance between the two keys at the points where they were struck by the pendulum was measured with a micrometer screw, and the corresponding time of charge could then be computed with great accuracy. By this method we were able to measure the time of charge in ten-thousandths of a second for any length of time from 0.0006 to 0.3 of a second. Below 0.0006 second the torsional vibration of the pendulum affected the accuracy of the time measurement. The time necessary for the lever of key K_1 to pass from the lower contact to the upper was appreciable. This error was eliminated by adjusting the distance K_1–K_2 until no deflection resulted, and then applying this distance as a correction to the distances as measured.

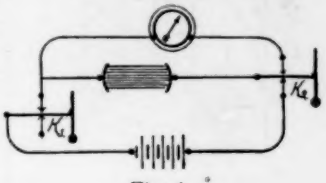


Fig. 1.

Observations were made with three different charging potentials to indicate any relation that might exist between the rate or amount of absorption and the potential difference.

A general idea of the data, Table I., may be obtained more easily from the curves, Fig. 2, where the abscissæ represent time of charge and the ordinates the corresponding deflections of the ballistic galvanometer.

[1] Carhart, PHYSICAL REVIEW, Vol. II., p. 392; or Carhart and Patterson's Electrical Measurements, p. 106.

These deflections are, of course, proportional to the quantities Q, when corrected to $2 \sin \frac{\theta}{2}$, as they should be for absolute values. Since, however, the effect of such correction would only be to reduce each deflection about two millimeters, the ratio of the highest to the lowest value for any particular curve would not be appreciably affected.

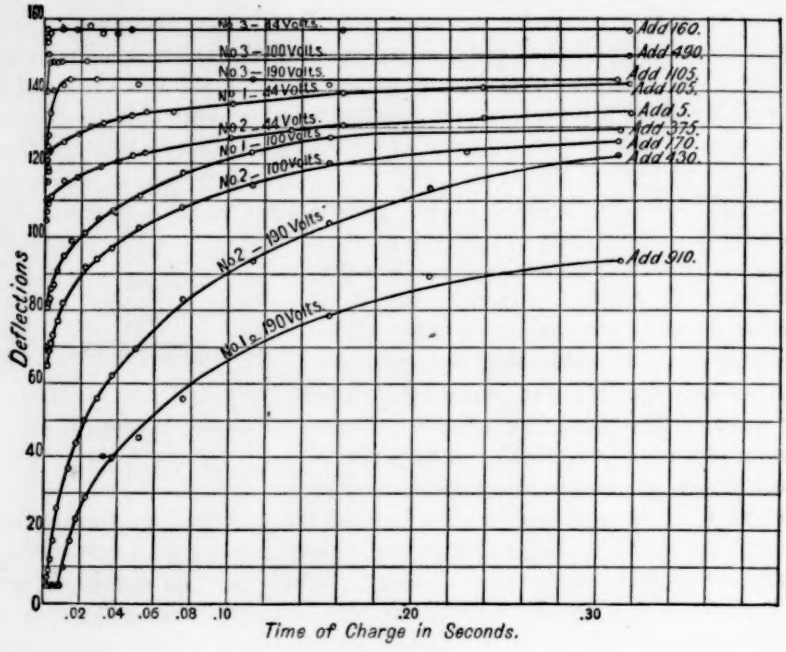


Fig. 2.

Time of charge.	Deflections at 44 volts.			Time of charge.	Deflections at 44 volts.		
	No. 1.	No. 2.	No. 3.		No. 1.	No. 2.	No. 3.
seconds				seconds			
0.0006	220.0	110.0	314	0.0409	237.0	126.0	316
0.0014	223.0	119.0	315	0.0486	238.0	127.0	317
0.0020	224.0	110.0	317	0.0560	239.0	128.0	—
0.0036	229.0	116.0	316	0.0714	239.5	129.0	—
0.0110	231.0	120.0	317	0.1023	241.0	132.0	—
0.0185	233.0	121.0	317	0.1636	244.5	135.5	317
0.0260	235.0	123.0	318	0.2390	246.0	137.5	—
0.0335	236.0	124.0	316	0.3196	247.0	139.0	317

Time of charge.	No. 1.		No. 2.		No. 3.	
	100 volts.	190 volts.	100 volts.	190 volts.	100 volts.	190 volts.
0.0015	456	825.0	235.0	—	630	—
0.0022	460	915.0	240.0	435.0	640	1230.0
0.0029	458	915.0	239.0	438.0	638	1233.0
0.0037	461	915.0	241.0	442.5	638	1239.0
0.0051	462	915.0	243.0	447.0	638	1245.0
0.0074	466	915.0	247.0	456.0	—	1245.0
0.0111	470	919.5	252.0	462.0	—	1246.5
0.0148	474	927.0	257.0	468.0	—	1248.0
0.0224	476	939.0	262.0	480.0	638	1246.5
0.0299	480	945.0	264.0	486.0	—	1245.0
0.0374	482	949.5	267.0	493.5	—	1246.5
0.0523	486	955.5	273.0	499.5	—	1245.0
0.0754	492	966.0	278.5	513.0	—	1245.0
0.1145	498	982.5	284.0	523.5	—	1248.0
0.1560	502	988.5	290.0	534.0	—	1248.0
0.2300	500	999.0	293.0	543.0	640	1248.0
0.3120	504	1003.5	296.0	552.0	640	1248.0
5.0000	524	1050.0	314.0	579.0	640	1257.0

Distance of scale = 110 cm.

Discussion of Results.

The data and curves show: (1) that the rapidity of absorption varies greatly for the different condensers; (2) that it varies with the potential difference; and (3) that the quantity absorbed after the first 0.005 second of charge is not strictly proportional to the potential difference. The total quantity absorbed cannot be determined, since absorption begins instantaneously upon closing the circuit. Steinmetz states the following law: Condensers having solid dielectrics should absorb under an alternating electromotive force an amount of energy proportional to the square of the potential difference. This has been shown experimentally to be approximately true within a wide range by J. Sahulka.[1] In our case, however, the time of discharge is so long that the above law cannot be applied.

The rapidity with which No. 3 absorbs its full charge indicates a very different dielectric than is found in the other two. The chief difference probably lies in the thickness of the insulation. The per cent of full charge that is absorbed after the first 0.005 second is, at 190 volts, by the Stanley condenser equal to 0.95 per cent; by the paraffin, 22.80 per cent; by the mica, 12.86 per cent.

[1] Wiener Sitz. Ber., Vol. 102.

This would seem to indicate that the quantity absorbed varies much more rapidly than in exact inverse ratio to the thickness, because this would make the paraffin insulation about twenty-five times as thick as that of the Stanley. This ratio of thickness is, however, possible.

The data show also that for short periods the value of Q is not strictly proportional to the potential difference. For example, take the condenser No. 2 with $t = 0.01$ second. The ratio of Q for 190 volts to Q for 100 volts is not 1.9, but is 1.76. At 190 volts the ratio of the full-charge capacity of No. 3 to the full-charge capacity of No. 2 is equal to 2.16, while for a charge period of 0.01 second the ratio is 2.62. The corresponding ratios of No. 1 to No. 2 are 1.81 and 1.99, respectively. These ratios bring out again the difference in the rate of absorption between the three condensers. It is apparent that the capacity of a condenser may be very different in an alternating-current circuit from its value when determined by full-charge methods. A change in the frequency of the alternations might easily cause an appreciable change in the apparent capacity.

This method could well be used to study the rate at which the different dielectrics give up their absorbed charges by changing the connections. It would then be interesting to combine the two and limit both charge and discharge to an equal period.

UNIVERSITY OF ILLINOIS,
DEPARTMENT OF ELECTRICAL ENGINEERING,
July, 1896.

NOTE ON THE OSMOTIC THEORY OF THE VOLTAIC CELL.

BY H. M. GOODWIN.

IN a recent paper on "The Chemical Potential of the Metals"[1] Mr. Bancroft, from certain experiments of his own, and from the investigations of Paschen on dropping electrodes, and of others, concludes that, "*first*, the potential difference between a metal and an electrolyte is not a function of the concentration of the salt solution, nor of the positive ion, except in certain special cases; *second*, it is a function of the electrode, of the negative ion, and of the solvent," etc. Without quoting further, these conclusions will be seen to be so contradictory to the well-established theory of Nernst and Ostwald that, in view of the mass of experimental evidence published in confirmation of this theory during the last few years, a serious consideration of them must seem superfluous. I wish to point out and show, however, that certain predictions of the author, on which he

[1] PHYSICAL REVIEW, Vol. III., 250, 1896.

bases a criticism of the results published by me on the electrometric determination of the solubility of difficultly soluble salts,[1] are in direct contradiction with facts, and that, therefore, the objections raised are ungrounded.

In the article referred to I have calculated the solubility of silver chloride, bromide, and iodide from measurements of the electromotive force of elements of the form —

$$\mathrm{Ag}\left|\, x\ \mathrm{AgNO_3}\,\right|\begin{matrix} x\ \mathrm{KCl} \\ \mathrm{AgCl}\end{matrix}\left|\,\mathrm{Ag}.\right.$$

The fundamental formula for all reversible cells applies to this element, its electromotive force E being given by the formula

$$E=\frac{RT}{e_0}ln\frac{p_1}{p'},$$

where p_1 and p' are the partial osmotic pressures (or concentrations) of the *kations* at the two electrodes, R the gas constant, T the absolute temperature, and e_0 the electrochemical equivalent. By Nernst's solubility principle the product of the silver and chlorine ions must be constant at the second electrode (electrode of the second kind) ; *i.e.*

$$p'(p'+p_2)=s^2,$$

where s is the solubility of silver chloride in water, and p_2 the concentration of the chlorine ions coming from the potassium chloride. Since p_2 is very great compared with p', we have, approximately,

$$p'=\frac{s^2}{p_2},$$

or

$$E=\frac{RT}{e_0}ln\frac{p_1p_2}{s^2},$$

from which s may be computed. In the deduction of this formula it is assumed that the electrolytic solution pressure of the electrodes is eliminated, and that the fundamental law of the osmotic theory of the cell holds true ; namely, that the potential difference between a metal and a liquid is determined by the *kation* concentration of the solution and is independent of the anion concentration.

Mr. Bancroft, however, questions the validity of this law — states, in fact, just the reverse of it. He bases his reasoning on the well-known fact that metals like mercury (which form insoluble halogen salts) show a different P.D. according to the soluble halogen salt with which they are in contact. Thus the absolute P.D. between mercury and a normal solution of potassium chloride, bromide, and iodide are, according to Paschen's[2] results with

[1] Zeitsch. für Phys. Chem., 13, 641, 1894; Technology Quarterly, 8, 166, 1895.

[2] Paschen, Wied. Ann., 43, 590, 1891.

dropping electrodes, 0.539, 0.483, and 0.400 volts respectively. Mr. Bancroft is apparently unable to see that such electrodes are practically electrodes of the second kind.

He says (p. 257): "If the potential difference between mercury and potassium chloride or potassium bromide solutions be due to the amount of mercury as ion which has gone into solution, we must say that the amount varies as we change from potassium chloride to potassium bromide [certainly it does], or, in other words, that the negative ion has an effect." In regard to the last part of this sentence I have shown very conclusively that the effect of the *anion* is in all cases of electrodes of the second kind an *indirect* but calculable one, inasmuch as their concentration determines by Nernst's solubility principle the concentration of the kations. Farther on he says: "I do not see that the relative solubilities of mercurous chloride and bromide can be used to help out matters, because we do not have a saturated solution at all." But this is practically what we do have, as is shown by the fact that the addition of a depolarizer (*e.g.* as in the normal electrode) does not appreciably alter the P.D. As a matter of fact, the above-cited results are in complete accord with Nernst's theory and might have been predicted from it. Since the iodides are less soluble than the bromides, and these again than the chlorides, by the solubility principle the kation concentration must diminish in the same order while the *anion* concentration remains practically constant, whence the decrease in the P.D.

Moreover, from a purely experimental standpoint, no more conclusive proof of the independence of the P.D. of the anion could be desired than that furnished by Neumann.[1] He measured the P.D. between thallium and over twenty different thallium salts, both organic and inorganic (including the chloride), and found in all cases the same value to within about 0.001 volt. Yet Mr. Bancroft will not be convinced by these figures of the fallacy of his law, since Neumann did not include in his measurements thallium bromide and iodide, the two salts whose slight solubility precluded their use for electrodes of the first kind.

As further evidence of the confounding of electrodes of the first and second kind, Mr. Bancroft applies conclusions deduced from the latter to the former. On page 260 he says: —

"If we consider the cell $Zn|ZnC_2|ZnBr_2|Zn$, the two solutions being assumed to be of the same concentration and dissociation and the wandering velocity of the bromine ion being further assumed to be identical with that of the chlorine ion, we should expect an electromotive force of 0.08 volt." With the bromide replaced by the iodide an electromotive force of 0.152 volt would be "expected." By reason of my failure to take this fact into account, my computation of the solubility of the silver halogens is, in his

[1] Zeitsch. f. Phys. Chem., 14, 225, 1894.

opinion, of no significance. Now if Mr. Bancroft had but made an experiment or two on cells of the above type, he would have found that instead of his predicted results the electromotive force both of the chloride-bromide and of the chloride-iodide cell is practically zero,—just as the osmotic theory requires (since the concentration of the zinc ions [the *kations*] at both electrodes is practically the same).

In the following table are given the results of some measurements I have made on cells of this type, which, aside from their bearing on Mr. Bancroft's statements, are of interest as furnishing additional evidence of the absolute confidence with which one may predict results from the osmotic theory. The halogen solutions were standardized by Vollard's method and then made up to the desired strength. The electrodes were liquid amalgams prepared by electrolyzing pure salt solutions of the metals over pure mercury kathodes. The cells used were of the H form, similar to those described in my previous paper.

Measurements were made by the usual Poggendorff method, exact compensation being obtained on a slide wire bridge by a capillary electrometer sensitive to 0.0001 volt. The apparatus was calibrated against a Clark cell from the Reichsanstalt. Measurements were made at the room temperature, which varied from 18° to 22° C. The values given are the mean of a series of measurements on three or four independent elements. The electromotive force was nearly constant from the start to within 0.001–0.002 volt.

TABLE I.

Cell.	Concentration 0.1 normal.	Concentration 0.05 normal.	Concentration 0.01 normal.
$ZnCl_2$–$ZnBr_2$	0.0030 volt	0.0021 volt	0.0023 volt
$ZnCl_2$–ZnI_2	0.0025	0.0019	0.0021

It is seen that the electromotive force of both elements is not only nearly the same but also practically zero, exactly as the osmotic theory requires. The 0.002 volt observed is probably due to the P.D. at the liquid junction. It is of a negligible amount compared with the 0.15 volt predicted by Mr. Bancroft. It need hardly be pointed out that the observed independence of the electromotive force of the absolute concentration is also a verification of the theory. These experiments, like those of Neumann, prove conclusively that in these reversible cells the *anion has absolutely no effect* on the electromotive force.

I give also some measurements on similar reversible cadmium cells, which

are not without interest. The electromotive force of these cells should of course also be zero, provided the assumption regarding the equal dissociation of the salts holds true. This, however, is well known, both from freezing-point determinations and conductivity measurements, *not* to be the case. The halogen salts of cadmium are all dissociated to an abnormally small extent, and moreover to an unequal extent, the iodide being least, the bromide and chloride more dissociated. Hence, the chloride solution should contain more cadmium ions than either the bromide or iodide solutions, and hence be positive to them. The nitrate, on the other hand, is nearly normally dissociated, and contains therefore many more ions than the chloride, — hence in a chloride-nitrate cell the chloride solution should be negative. These predictions of the theory were found to be completely verified by experiment, as the following measurements show: —

TABLE II.

$CdCl_2$–$CdBr_2$	+0.005 volt
$CdCl_2$–CdI_2	+0.015
$CdCl_2$–$Cd(NO_3)_2$	−0.024

The solutions were all 0.1 molecular normal.

The electromotive force of the chloride-iodide cell is no longer small and equal to that of the bromide cell, but three times greater; the reversal of the electromotive force when the nitrate is used as one electrolyte is also evident.

In view of these results, Mr. Bancroft's objections to my interpretation of the results on silver halogen electrodes are evidently unfounded. I am utterly unable to understand why he should have passed over in silence the most striking and unquestionable proof I gave of the theory of difficultly soluble depolarizers, namely, the complete agreement of the electromotive force of the element,

$$\mathrm{Tl}\left|\begin{matrix}\mathrm{TlCl}\\ \text{in KCl}\end{matrix}\right|\left|\begin{matrix}\mathrm{TlCl}\\ \text{in KBr}\end{matrix}\right|\mathrm{Tl},$$

calculated from the solubility of the depolarizers *analytically* determined, with that actually observed, a result absolutely impossible on the assumptions of his theory.

In closing, it should be stated that the failure to discuss the other conclusions of Mr. Bancroft's paper does not imply an acceptance of them. In many cases their fallacy is as apparent as in the case here considered.

ROGERS LABORATORY OF PHYSICS,
MASSACHUSETTS INSTITUTE TECHNOLOGY,
June, 1896.

The Division of an Alternating Current in Parallel Circuits with Mutual Induction.[1]

By Frederick Bedell.

A DIVIDED circuit with mutual induction between the two branches is shown in Fig. 1, being the same as a transformer with the primary and secondary circuits connected in parallel. The electromotive force equations for the two circuits are similar, the internal electromotive forces in each being equal to the same impressed electromotive force. The electromotive force of mutual induction will be positive or negative according to the sense or direction in which the coils are connected. If the coils are connected as in Fig. 2, so that the ampere turns of the two coils assist each other, the electromotive forces of self and mutual induction will be of the same sign, and the coefficient of mutual induction will be positive. If the coils are connected so as to oppose each other, as in Fig. 3, the electromotive force of mutual induction will be opposite in sign to that of self-induction. The coefficient of mutual induction may accordingly be $+M$ or $-M$. Writing the electromotive force as a function of the time, we have the following equations: —

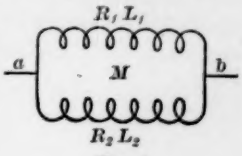


Fig. 1.
Divided circuit with mutual induction.

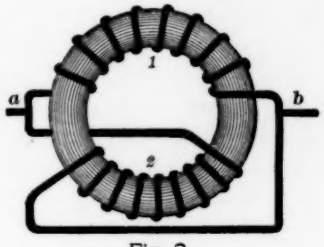


Fig. 2.
Coils additive.

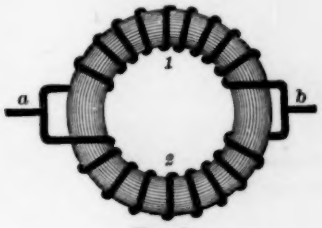


Fig. 3.
Coils opposed.

$$e = f(t) = R_1 i_1 + L_1 D i_1 \pm M D i_2; \quad (1)$$
$$e = f(t) = R_2 i_2 + L_2 D i_2 \pm M D i_1. \quad (2)$$

By differentiation, the above equations become

$$f'(t) = R_1 D i_1 + L_1 D^2 i_1 \pm M D^2 i_2;$$
$$f'(t) = R_2 D i_2 + L_2 D^2 i_2 \pm M D^2 i_1.$$

[1] A paper read at the Liverpool meeting of the British Association for the Advancement of Science, 1896.

Eliminating i_2 by determinants, we have

i_2	Di_2	D^2i_2	OTHER TERMS.
0	$\pm M$	0	$R_1i_1 + L_1Di_1 - f(t)$
0	0	$\pm M$	$R_1Di_1 + L_1D^2i_1 - f'(t)$
R_2	L_2	0	$\pm MDi_1 - f(t)$
0	R_2	L_2	$\pm MD^2i_1 - f'(t)$

$= 0.$

Canceling out the first column and third row, as indicated by fine type, we obtain

$$M^2[\pm MD^2i_1 - f'(t)] \mp MR_2[R_1i_1 + L_1Di_1 - f(t)] \mp ML_2[R_1Di_1 + L_1D^2i_1 - f'(t)] = 0. \quad (3)$$

From this equation the value for the current i_1 is obtained: —

$$i_1 = \frac{R_2f(t) + (L_2 \mp M)f'(t)}{(L_1L_2 - M^2)D^2 + (R_1L_2 + R_2L_1)D + R_1R_2}. \quad (4)$$

A similar expression is found for i_2.

For an harmonic electromotive force

$$e = f(t) = E \sin \omega t;$$
$$f'(t) = E\omega \cos \omega t.$$

Since $D^2 \sin \omega t = -\omega^2 \sin \omega t$, we may write $-\omega^2$ for D^2.

In equation (4) we may make these substitutions for $f(t)$, $f'(t)$, and D^2. By combining the sine and cosine terms into one term, and multiplying numerator and denominator by D, we have

$$i_1 = \frac{DE\sqrt{R_2^2 + (L_2 \mp M)^2\omega^2} \sin\left(\omega t + \text{arc tan}\frac{(L_2 \mp M)\omega}{R_2}\right)}{\alpha D - \omega\beta}; \quad (5)$$

where

$$\alpha = R_1R_2 - \omega^2(L_1L_2 - M^2),$$
$$\beta = \omega(R_1L_2 + R_2L_1).$$

To free equation (5) from the operator D, perform the operation D as indicated in the numerator (by differentiating the numerator), and multiply numerator and denominator by $\alpha D + \omega\beta$. Substitute $-\omega^2$ for D^2 in the denominator and again perform the operation D in the numerator. We thus obtain an expression for i_1 which is free from D; this may be written in the following form: —

$$i_1 = I_1 \sin(\omega t + \phi_1); \quad (6)$$

where
$$I_1 = \frac{E}{\sqrt{\alpha^2+\beta^2}\Big/\sqrt{R_2^2+(L_2 \mp M)^2\omega^2}}. \tag{7}$$

$$\phi_1 = -\arctan\frac{\beta}{\alpha} + \arctan\frac{(L_2 \mp M)\omega}{R_2}. \tag{8}$$

Similarly, for the current in the second branch,

$$i_2 = I_2 \sin(\omega t + \phi_2); \tag{9}$$

where
$$I_2 = \frac{E}{\sqrt{\alpha^2+\beta^2}\Big/\sqrt{R_1^2+(L_1 \mp M)^2\omega^2}}. \tag{10}$$

$$\phi_2 = -\arctan\frac{\beta}{\alpha} + \arctan\frac{(L_1 \mp M)\omega}{R_1}. \tag{11}$$

The ratio of the two currents is

$$\frac{I_1}{I_2} = \frac{\sqrt{R_2^2+(L_2 \mp M)^2\omega^2}}{\sqrt{R_1^2+(L_1 \mp M)^2\omega^2}}. \tag{12}$$

Their phase difference is

$$\phi_1 - \phi_2 = \arctan\frac{(L_2 \mp M)\omega}{R_2} - \arctan\frac{(L_1 \mp M)\omega}{R_1}. \tag{13}$$

Where the coils are opposed and nearly similar the angle of phase difference between the currents depends largely upon the amount of magnetic leakage.

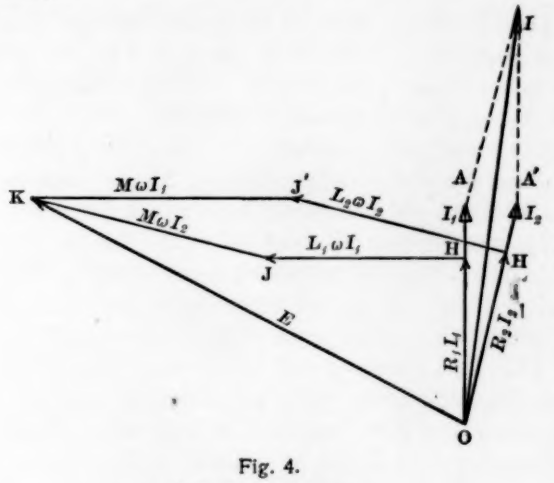


Fig. 4.

Coils additive; M positive.

The diagram for the electromotive forces in a divided circuit in which the effects of self and mutual induction are additive is shown in Fig. 4. The two currents are I_1 and I_2, respectively, the main current being their vector sum I.

In branch one, OH is the power electromotive force (in the absence of branch two); HJ and JK are the electromotive forces of self and mutual induction, being at right angles to the currents I_1 and I_2, respectively. The corresponding electromotive forces for the second circuit are shown in the same diagram. The sum of the several electromotive forces in either circuit add up to E, the impressed electromotive force.

Ordinarily the branch current and the main current would lag behind the impressed electromotive force by a large angle approaching 90°.

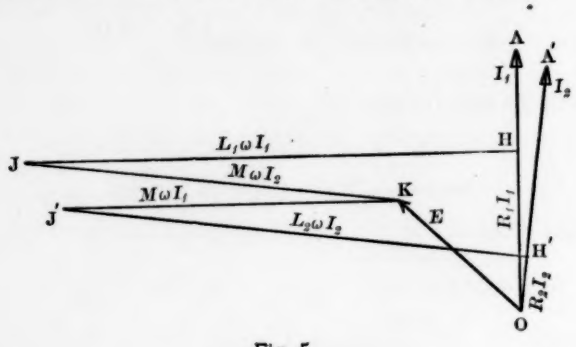


Fig. 5.

Coils opposed: M negative.

When the two circuits are identical, the branch currents I_1 and I_2 would have the same magnitude and direction; the points H′ and J′ would coincide with the points H and J, respectively. An inspection of the figure will show that for this case, in the absence of magnetic leakage, the effect of the mutual induction would be to double the tangent of the angle of lag.

Figure 5 shows the corresponding diagram for the case in which the electromotive forces of self and mutual induction are opposed. The current I_1 produces an electromotive force HJ in the first branch, and J′K in the second branch; these electromotive forces being at right angles to the current I_1, and opposite to each other in direction, on account of the sense in which the two coils are connected. Similarly, H′J′ is opposite in direction to JK. The effects of self and mutual induction consequently tend to neutralize each other. The electromotive force OK, required to cause the currents I_1 and I_2 to flow, is accordingly made less on account of the mutual induction, and would be reduced to the value of the ohmic electromotive force in the case of two similar coils wound oppositely. In

this case the angle of lag would be reduced to zero, and the coil would be non-inductive.

The equivalent resistance and self-induction for the two coils together, whether they are additive or opposed, may be found by resolving E into two components, one in the direction of the main current, and the other at right angles to it. These components will be equal to $R'I$ and $L'\omega I$, respectively. Their magnitudes may be obtained graphically, and from them the values of the equivalent resistance R' and the equivalent self-induction L'. The equivalent resistance and self-induction of either branch may be obtained in the same manner.

The conclusions relating to the special case of two identical coils wound without magnetic leakage, stated above in connection with the graphical construction, may be reached by substituting in the formulæ the values $R_1 = R_2 = R$; and $L_1 = L_2 = \pm M = L$. Also, $\beta \div \alpha = 2 L\omega \div R$. The two cases are as follows: —

When M is positive. — When M is positive, the coils being wound in the same direction,

$$\phi = -\text{arc tan}\frac{2 L\omega}{R} + \text{arc tan } 0 = -\text{arc tan}\frac{2 L\omega}{R}. \qquad (14)$$

The current in each branch is

$$I_1 = I_2 = \frac{E}{\sqrt{R^2 + (2 L\omega)^2}}. \qquad (15)$$

For this case, therefore, the effect produced is the same as though the mutual induction were zero and the self-induction of each circuit doubled, the tangent of the angle of lag being doubled and each current being diminished accordingly.

The main current is

$$I = I_1 + I_2 = \frac{2 E}{\sqrt{R^2 + (2 L\omega)^2}} = \frac{E}{\sqrt{\left(\frac{R}{2}\right)^2 + L^2\omega^2}}, \qquad (16)$$

which is the same that would flow in a single coil, with the same self-induction and half the resistance as either branch.

When M is negative. — When the coils are identical and opposed,

$$\phi = -\text{arc tan}\frac{2 L\omega}{R} + \text{arc tan}\frac{2 L\omega}{R} = 0; \qquad (17)$$

$$I_1 = I_2 = \frac{E}{R}. \qquad (18)$$

Each coil acts in this case as though non-inductive, the magnitude of the current being in accordance with Ohm's law, and the angle of lag being zero.

Cases where the two coils are not identical may be treated by substituting particular values for the resistance and coefficients of induction in the general equations.

ITHACA, N.Y., June, 1896.

ON THE SPECIFIC GRAVITY AND ELECTRICAL CONDUCTIVITY OF THE NORMAL SOLUTIONS OF SODIUM AND POTASSIUM HYDROXIDES, AND HYDROCHLORIC, SULPHURIC, NITRIC, AND OXALIC ACIDS.

BY E. H. LOOMIS.

THE various tables of specific gravity of these common alkaline and acid solutions differ in some cases so considerably that the attempt to compute the specific gravity of a particular solution, of known strength, by use of the tables, results in much uncertainty.

This uncertainty has made it desirable to measure the specific gravity of certain normal solutions about which the most doubt exists. I have accordingly undertaken to prepare such solutions of NaOH, KOH, HCl, HNO_3, H_2SO_4, and $(COOH)_2$, for the purpose of measuring their specific gravity. I have also taken this opportunity to measure their electrical conductivity.

The various solutions were prepared by titration. The titration standards were normal solutions of sodium carbonate and oxalic acid whose preparation will be first described.

Normal Sodium Carbonate. — Sodium acid carbonate ($NaHCO_3$, Trommsdorff, c.p.) was glowed, and thus converted into Na_2CO_3. A saturated solution of this product was then treated with a current of pure CO_2 until the precipitation of $NaHCO_3$ was complete. This precipitated $NaHCO_3$ was then carefully heated at a temperature slightly under red glow until its weight became constant. The Na_2CO_3 thus obtained was deemed sufficiently pure for the given purpose.

The molecular weight of this salt (O = 16) is 106.12. Thus a normal solution requires 53.06 g. per liter of the solution.

The liter flask employed at 18° C. contained 1000 c.c.

A simple calculation shows that such a flask should hold apparently 997.667 g. of water whose temperature is 18° C. when the weighing is made in the air with brass weights. The mark on the flask was fixed in

this way. The volume of such a flask is a true liter, *i.e.* that of 1000 g. of water at 4° C.

Normal Oxalic Acid Solution. — The c.p. acid was purified by recrystalizing twice from water, and, finally, by recrystalizing from dilute alcohol, according to Mohr. The crystals were then freed from the mother liquor, first, by a mechanical process, and, finally, by rolling and pressing between folds of filter paper.

The acid thus prepared still left a faint stain when volatilized on platinum foil. It was deemed, however, sufficiently pure for the purpose. The molecular weight of oxalic acid $(COOH)_2$, $2\,H_2O$ is 108. Accordingly, 54 g. were dissolved in water, and the solution diluted to a liter, at 18° C. These normal solutions of Na_2CO_3 and $(COOH)_2$ were then balanced against each other, and found to be equivalent. Thus the accuracy of each was confirmed.

The other normal solutions were prepared by titration with one or the other of these directly, or with some normal solution which had been directly standardized with them.

All of the titrations were performed by Mr. Hulett of the Princeton Chemical Laboratory, and I wish here to express my deep obligation to him for the great care with which this work was done, and for his additional assistance in the preparation and purification of many of the materials.

Sodium and Potassium Hydroxide. — The hydroxides were prepared by direct union of the metals with water in a silver vessel.

The metals were carefully freed from "scale" in the open air at about 0° C. The solutions were filtered through asbestos.

The NaOH solution was perfectly colorless, while the KOH solution, when concentrated, retained a slight straw color which indicated traces of organic matter. All reasonable precautions were taken to exclude CO_2 from the solutions during these operations.

Both the NaOH and KOH solutions were brought to normal strength by titration with a normal solution of H_2SO_4 which had already been standardized directly against the normal Na_2CO_3.

In these and the subsequent titrations, methyl orange was used as indicator, and, whenever possible, a second titration, with phenolphtalein as indicator, was made for the sake of checking the work.

It should be added that the final reduction of the given solution to normal strength was made by using a one-tenth normal solution of the particular standard with which the comparison was made.

After the required amount of water or compound had been added, a final titration was made to insure against any possible errors.

Hydrochloric Acid. — The c.p. acid (Baker and Adamson) was heated, and the expelled HCl gas was conducted through a platinum tube into

water. The HCl solution was then diluted to normal strength by titration with the normal NaOH. It was then compared with the standard Na_2CO_3 directly, and found to be in exact balance.

Nitric Acid. — The c.p. acid (Baker and Adamson) was found to be free from chlorine and was then redistilled through platinum.

The acid was then reduced to normal strength by direct titration with the standard Na_2CO_3.

Sulphuric Acid. — The c.p. acid of Baker and Adamson was deemed of sufficient purity for the purpose. It was titrated directly with the standard Na_2CO_3.

Determination of Specific Gravity.

Water at 4° C. was taken as unity, and the temperature of the solutions was uniformly 18° C. The method employed was that of Sprengel, modified as I have already described in a former paper.[1]

The Electrical Conductivity.

The measurements were made in accordance with the Kohlrausch method. The resistance vessel was of the double type (Kohlrausch, *Leitfaden d. Physik*, Leipzig, 1892, 4th figure, p. 304).

Its "resistance capacity" was found (adopting the Kohlrausch value for normal NaCl as 696.10^{-8}) to be 0.00158 Hg units.

The vessel and contents were kept at 18° C. ± 0°.05 by immersion in a water bath kept carefully at this temperature for about thirty minutes before the measurement was made.

The Results.

In the following table the specific gravity of the various solutions is found in column 2, and the electrical conductivity K, multiplied by the factor 10^7 is found in column 3.

Conductivity of mercury at 4° C. is taken as standard.

1 Compound.	2 Sp. Gr. $\frac{18°}{4°}$.	3 $K \cdot 10^7$.	1 Compound.	2 Sp. Gr. $\frac{18°}{4°}$.	3 $K \cdot 10^7$.
NaOH	1.0418	145	HNO_3	1.0324	278
KOH	1.0481	170	H_2SO_4	1.0306	183
HCl	1.0165	279	$(COOH)_2$	1.0199	55

[1] Loomis, PHYSICAL REVIEW, Vol. III., p. 270, 1896.

In addition to the NaOH solution, of which the measurements are given in the table, a second normal solution was prepared, by Mr. Hulett, by two successive purifications of Trommsdorff's c.p. NaOH by the well-known ethyl-alcohol process. The entire process was conducted in air freed from CO_2.

The product was perfectly colorless, and nearly transparent.

This hydroxide is believed to be as nearly pure as the alcohol method permits.

The specific gravity of this normal solution is 1.0417, and the electrical conductivity is 146.10^7. These results are not in agreement with those found for the solution made directly from the metallic sodium. The latter method undoubtedly yields the purer hydroxide, and the results for this are given in the table.

PHYSICAL LABORATORY, PRINCETON UNIVERSITY.

NOTES.

The Buffalo Meeting of the American Association for the Advancement of Science. — At the Buffalo meeting of the Association, which was held August 24 to 29, the attendance was small. The programme in Physics, as has been the case at many of the smaller recent meetings, did not, however, suffer from the smallness in general attendance. While there were no papers of supreme importance, the list was an interesting one throughout. The attendance upon the sittings of the section was excellent, and the number of physicists present at the meeting who are actively engaged in the research was noticeably large.

The title of Chairman Mees' address was "Electrolysis and Some Outstanding Problems in Molecular Dynamics."

The following is the list of papers presented in Section B: "Polarization and Internal Resistance of a Galvanic Cell," by B. E. Moore; "The Lead Storage Cell," by B. E. Moore; "A Theory of Galvanic Polarization," by W. S. Franklin and L. B. Spinney; "On the Counter Electromotive Force of the Electric Arc," by W. S. Franklin; "On the Element of Diffraction in Fresnel's Experiments with Two Mirrors and with the Bi-prism," by Ernest R. von Nardroff; "Segmental Vibrations in Aluminum Violins," by Alfred Springer; "Preliminary Note on a Proposed New Standard of Light," by Clayton H. Sharp; "A Photographic Study of the Roentgen Rays," by W. A. Rogers; "Note on the Duration of the X-Ray Discharge in Crookes' Tubes," by Benjamin F. Thomas; "Preliminary Communication concerning the Anomalous Dispersion of Quartz for Infra-red Rays of Great Wave-length," by Ernest F. Nichols; "An Experimental Study of the Charging and Discharging of Condensers," by F. E. Millis; "Notes on Certain Physical Difficulties in the Construction of Modern Large Guns," by W. LeConte Stevens; "On the Photographic Trace of the Curves described by the Gyroscopic Pendulum," by Ernest Merritt; "On the Distribution of High Frequency Alternating Currents throughout the Cross-Section of a Wire," by Ernest Merritt; "On the Compactness of a Beam of Light," by Ernest R. von Nardroff; "Some Points in the Mechanical Conception of the Electromagnetic Field," by W. S. Franklin; "Mechanical Models of the Electric Circuit," by Brown Ayres; "Graphical Treatment of Alternating Currents in Branching Circuits," by Henry T. Eddy; "Description and Exhibition of a Convenient Form of the 'Interferential Comparer,' and of an Interferential Caliper Attachment for Use in

Physical Laboratories," by W. A. Rogers; "Description and Exhibition of a Bench Comparator for General Use in Physical Laboratories," by W. A. Rogers; "On the Rule for the Dynamo and Motor," by Alexander Macfarlane; "Note on the Effect of Odd Harmonics upon the Virtual Values of Periodically Varying Quantities," by Frederick Bedell and James E. Boyd; "Experimental Determination of the Relative Amounts of Work done in changing the Lengths of Two Metal Bars under the Same Thermal Conditions, by an Envelope of Heated Air, and by Pure Radiations in a Vacuum," by W. A. Rogers; "A New Alternating-Current Curve Tracer," by Edward B. Rosa; "On a Piece of Apparatus constructed by Joseph Henry," by C. E. West; "Visible Electric Waves," by B. E. Moore; "Electrical Waves in Long Parallel Wires," by A. D. Cole; "The Influence of a Static Charge of Electricity on the Surface Tension of Water," by Edward L. Nichols and John Anson Clark; "Determination of the Specific Heats of Nitrogen by Adiabatic Expansion," by W. S. Franklin and L. B. Spinney; "The Analysis of Vowel Sounds by Means of the Sympathetic Vibrations of a Rigid Body," by L. B. Spinney; "Description and Exhibition of a Portable Apparatus for recording Curves of Alternating Currents and Electromotive Force," by H. J. Hotchkiss.

The officers for 1897 are: —

President: Wolcott Gibbs, of Newport, R.I.

Vice-Presidents: A. Mathematics and Astronomy, W. W. Beman, of Ann Arbor, Mich.; B. Physics, Carl Barus, of Providence, R.I.; C. Chemistry, W. P. Mason, of Troy, N.Y.; D. Mechanical Science and Engineering, John Galbraith, of Toronto, Canada; E. Geology and Geography, I. C. White, of Morgantown, W.Va.; F. Zoölogy, G. Brown Goode,[1] of Washington, D. C.; G. Botany, George F. Atkinson, of Ithaca, N.Y.; H. Anthropology, W. J. McGee, of Washington, D.C.; I. Social and Economic Science, Richard T. Colburn, of Elizabeth, N.J.

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General Secretary: Asaph Hall, Jun., of Ann Arbor, Mich.

Secretary to the Council: D. S. Kellicott, of Columbus, Ohio.

Secretaries of the Sections: A. Mathematics and Astronomy, James McMahon, of Ithaca, N.Y.; B. Physics, Frederick Bedell, of Ithaca, N.Y.; C. Chemistry, P. C. Freer, of Ann Arbor, Mich.; D. Mechanical Science and Engineering, John J. Flather, of Lafayette, Ind.; E. Geology and Geography, C. H. Smyth, Jun., of Clinton, N.Y.; F. Zoölogy, C. C. Nutting, of Iowa City, Iowa; G. Botany, F. C. Newcombe, of Ann Arbor, Mich.; H. Anthropology, Harlan I. Smith, of New York, N.Y.; I. Social and Economic Science, Archibald Blue, of Toronto, Canada.

[1] Deceased Sept. 6, 1896.

Treasurer: R. S. Woodward, of New York, N.Y.

The next annual meeting will be held in Detroit during the week preceding the British Association meeting in Toronto.

The British Association for the Advancement of Science.— Under the presidency of Sir Joseph Lister, the sixty-sixth annual meeting of the Association was held in Liverpool, September 16–23, with an attendance of over three thousand. The interest in the meetings of the Physics Section (A), presided over by Prof. J. J. Thomson, was particularly due to the vigorous discussions by a score of leading physicists, Lord Kelvin being chief, his comments, ingenuous and pertinent, never allowing an obscure point to pass, and ever stimulating the scientific pulse of the meeting.

The presidential address by J. J. Thomson, and the papers for two days, dealt almost solely with Roentgen and cathode rays. This prolonged discussion, in which Lenard and Bjerknes as well as English physicists took part, characterized the meeting, but lead to no generally accepted results.

On the recommendations of the committee appointed at Ipswich with Sir Douglas Galton as chairman, the Association voted to take active measures to secure from the government the necessary appropriation for the establishment of a National Physical Laboratory for the more accurate determination of physical constants and for other quantitative research, similar in many respects to the Physikalische-technische Reichsanstalt established and supported by the German government. Dr. Kohlrausch took part in the discussion of the requirements of such an institution. It is suggested that the laboratory be erected on the grounds of the Kew Observatory at Richmond Park.

After an animated discussion, the report of the Electrical Standards Committee was adopted, recommending the *erg* as the absolute unit of heat and 4.2×10^7 ergs as a secondary unit to be called the *calorie*. It is thus proposed to establish thermal units independent of thermometry.

The evening lecture to workingmen was admirably given by Dr. Fleming, his subject being "The Earth a Great Magnet."

The following papers were read in Section A: Isaac Roberts, "On the Evolution of Stellar Systems"; G. H. Darwin, "On Periodic Orbits"; P. Lenard, "On Cathode Rays"; J. J. Thomson and E. Rutherford, "On the Laws of Conduction of Electricity through Gases exposed to the Röntgen Rays"; A. W. Rucker and W. Watson, "On the Transparency of Glass and Porcelain to the Röntgen Rays"; S. P. Thompson, "On Hypophosphorescence"; S. P. Thompson, "On the Relation between Kathode Rays, X-Rays, and Becquerel's Rays"; H. H. F. Haysman, "Observations on the X-Rays"; Allan Cunningham, "Connection of Quadratic Forms"; H. M. Taylor, "On Great Circle Sailing"; S. H. Burbury, "On the

Stationary Motion of a System of Equal Elastic Spheres"; G. H. Bryan, "On Some Difficulties connected with the Kinetic Theory of Gases"; W. E. Plummer, "Comparison of the Results obtained from the Records of Robinson's, Osler's, and Dines's Anemometers"; A. Lawrence Rotch, "On the Exploration of the Upper Air by Means of Kites"; W. Hibbert, "On a One-volt Standard Cell with Small Temperature Coefficient"; W. H. Preece, "On Disturbance in Sub-Marine Cables"; Lord Kelvin, Magnus Maclean, and Alexander Galt, "On the Communication of Electricity from Electrified Steam to Air"; Lord Kelvin, J. T. Bottomley, and Magnus Maclean, "On Measurements of Electric Currents through Air at Different Densities down to One Five-Millionth of the Density of Ordinary Air"; Joseph Goold, "On Synchronisation of Sound Generators"; E. Rutherford, "On a Method of Detecting Electromagnetic Waves"; F. Bedell, "On the Division of an Alternating Current in Parallel Circuits with Mutual Induction"; E. H. Griffiths, "Note on the Measurement of Electrical Resistance"; S. A. Sworn, "Researches in Absolute Mercurial Thermometry"; Lord Kelvin, "On the Molecular Dynamics of Hydrogen Gas, Oxygen Gas, Ozone, Peroxide of Hydrogen, Vapor of Water, Water and Ice"; J. Chunder Bose, "On a Complete Apparatus for the Study of the Properties of Electric Waves"; W. M. Mordey, "Carbon Megohms for High Voltages"; W. M. Mordey, "On an Instrument for Measuring Magnetic Permeability"; G. H. Bryan, "On the Sailing Flight of Birds"; A. A. Rambaut, "On the Effect of Refraction on the Diurnal Movement of Stars, and a Method of allowing for it in Astronomical Photography"; R. Harley, "On the Stanhope Arithmetical Machine of 1780"; Elster and Geitel, "Photo-electric Sensitization of Salts by Kathode Rays"; A. P. Trotter, "A Direct-reading Form of Wheatstone Bridge"; W. N. Shaw, "The Total Heat of Water"; J. E. Keeler, "Measurements of the Velocity of Rotation of the Planets by the Spectroscopic Method"; L. A. Bauer, "On the Components Fields of the Earth's Permanent Magnetism"; F. T. Trouton, "The Duration of the X-radiation at Each Spark"; J. A. Harker and A. Davidson, "On Reostene, a New Resistance Metal"; R. Harley, "Results connected with the Theory of Differential Resolvents"; W. Barlow, "Homogeneous Structures and the Symmetrical Partitioning of them, with Application to Crystals"; J. Burke, "Change of Absorption accompanying Fluorescence."

Reports were submitted by committees on the following subjects: "On the Establishment of a National Physical Laboratory"; "On the $G(r, v)$ Integrals"; "On Bessel Functions and Other Mathematical Tables"; "On Meteorological Observations on Ben Nevis"; "On Solar Radiation"; "On Seismological Observations"; "On Meteorological Photographs"; "On the Comparison and Reduction of Magnetic Observations";

"On Electrical Standards (on Thermal Units)"; "On Magnetic Standards"; "On Electrolysis"; "On the Sizes of Pages of Periodicals."

The grants made amounted to £1355.

The Association meets next year at Toronto, August 18, under the presidency of Sir John Evans. American scientists will extend a hearty welcome to their British guests.

F. B.

NEW BOOKS.

Lehrbuch der Experimentalphysik. Von ADOLPH WÜLLNER. Fünfte vielfach umgearbeitete und verbesserte Auflage. Erster Band, "Allgemeine Physik und Akustik." Zweiter Band, "Die Lehre von der Wärme." Leipzig, B. G. Teubner, 1895 and 1896.

The publication of a carefully edited work which has for its aim the orderly presentation of the phenomena of physics, the judicious grouping of these phenomena according to their relationships, and the mathematical development of theory as far as it may be safely carried without allowing mathematics to dominate the physics, is not an event of everyday occurrence, and students of science should congratulate themselves upon the issue of a new edition of a work so well known and approved as the one under consideration.

There seems to be good ground for the belief that, of late years, the systematic study of physical phenomena has not received that attention its importance demands, and that mathematical physics and research work have claimed the student's time too early in his course. The existence of such a state of affairs can be accounted for by the very natural and commendable desire to produce as soon as possible a good piece of original work for publication or for a thesis, but it is responsible for much crude and immature work, and often fosters a spirit of conceit which the student's real attainments do not warrant.

Works on mathematical physics and laboratory manuals have been produced in abundance during the last ten years, but these, valuable as they are, do not supply the earliest want of the student. He needs an intimate acquaintance with the phenomena of nature and their relations. This, without doubt, can be gained most thoroughly and effectively at first by the study of text-books.

Without this fundamental knowledge the student's mathematical training loses half its value; for he wants that which gives him the ability to read the physical meaning of his equations, and his skill in the manipulation of apparatus lies idle or is misdirected through ignorance.

Wüllner's *Lehrbuch* is well adapted to the use of the young student who, having followed the general courses offered to undergraduates in our colleges, wishes to proceed with a thorough and systematic study of experimental physics.

The author takes little for granted, and treats elementary problems and describes the simplest instrumental appliances fully and in a manner which generally leaves little opportunity for criticism.

At the same time his subject is well written up to date, and includes a fair presentation of recent theory and experimental research.

As in previous editions, the text is supplemented by liberal and judicious reference to original papers.

These references in Vol. I. include publications to the end of 1892, and in Vol. II. to the end of 1893. This feature of the work gives it great value. English and American writers might well copy it more extensively.

It appears singular that the author finds it necessary to incorporate into the introductory chapter a little treatise thirteen and one-half pages long, explanatory of the methods and notation of the differential and integral calculus. It would seem that a person who was likely to use a work like the one under consideration could be assumed to possess a competent knowledge of elementary mathematics. The chapter is well done, however, as far as it goes. If its introduction is unnecessary, the error may be pardoned: it only makes a big book a little larger. It is not safe, however, to assume that the reading of this chapter will prepare the student for the mathematical work which follows in the body of the book. The reader will require a good working knowledge of the calculus, including some skill in handling differential equations, although in many cases the author gives in detail the steps by which he reaches his solution.

Among the commendable features of the work may be mentioned the liberal quotation of numerical tables giving actual experimental results which have been obtained in important investigations.

In many text-books these are omitted for want of room, and only single or average values are given. In such cases the student can form no idea of the accuracy of the work upon which conclusions are based. Every statement is absolute. There are no relative values, and incorrect notions are acquired as to what is proven and what is only highly probable. The illustrations also are excellent. They usually show actual apparatus instead of diagrammatic outlines, and in most cases a mechanic could build from them a working instrument which could be used without change for effective experimental work.

The two volumes of the fifth edition already published are not greatly changed in general appearance from those of the preceding issues. The paper is good, and the type and presswork leave nothing to be desired in a work of this kind. The corresponding volumes of the fourth edition appeared in 1882 and 1885, and it is interesting to compare them with the present issue and to note the thoroughness of the revision. We find as we should expect a liberal amount of new matter. The first volume is increased

from 848 to 1000 pages, and the volume on Heat from 825 pages to 919. We find few chapters in which material changes have not been made. Many sections have been rewritten, some transferred to more appropriate positions, and others have been omitted entirely. In the mathematical part of the work these changes are numerous.

In the fourth and preceding editions Vol. I. was devoted to General Physics and Sound; Vol. II. to Light; Vol. III. to Heat; and Vol. IV. to Electricity and Magnetism.

In the fifth edition this order is changed and the treatment of Light is reserved for the fourth volume, following Electricity.

This change is obviously made to prepare the way for a proper presentation of the electromagnetic theory of light.

When we come to examine the work in detail, we find that the author has discarded the gravitation unit of force for the absolute unit in his treatment of the mechanical problems in the first volume, and has promoted his section on the absolute system of measurements from its position as an appendix to a more honorable place in the first chapter on Mechanics. He has also introduced into the second chapter a ten-page section on the general equations of motion, with examples showing their application.

It is in the second division of the first volume — that which treats of the internal constitution of bodies and the phenomena dependent upon it — that we should expect to find the author's work of revision most amply illustrated. These three chapters on Solids, Liquids, and Gases are largely expanded by the addition of new matter and by the more complete presentation of theory. Among the additions we find quoted observations by Thompson on the variation of the coefficient of elasticity with an increasing load; by Röntgen, Voigt, Cornu, and Cantone, on the diminution of the cross-section of rods under tension; by Amagat and Cantone on cubic compressibility; by Tomlinson, Pisati, and others, on the change in the coefficient of elasticity with the temperature; Hertz' theory of hardness, with Auerbach's measurements in absolute units; and Boltzman's theory of internal friction, with experimental evidence bearing on the subject. Capillarity and surface tension are treated more fully than in the previous edition, and a new section is added on the kinetic theory of fluids, with its application to the theories of solution, osmotic pressure, and diffusion as developed by Van t' Hoff, Nernst, and Riecke. That part of the first volume which treats of wave motion and sound — subjects whose experimental side has received comparatively little attention of late years — appears in substantially the same form as in the fourth edition. The few pages which have been added are largely devoted to the mathematical development of the subject.

Volume II. is divided into five chapters, which, as in the fourth edition,

treat of the subdivisions of the subject in the following order: Expansion, Radiation and Conduction, Mechanical Theory of Heat, Specific Heat, Change of State, and Heat from Chemical Reactions.

The chapter on Thermometry has been enlarged by the addition of a section on the use of thermo-electric elements, especially in the case of extreme temperatures, and the author now includes the bolometer among the instruments employed in the study of radiant heat. Svanberg is credited with the invention of the method, and Langley is mentioned as using it thirty years later, and as giving the instrument its name. Contrary to his usual custom, the author does not describe the instrument as actually constructed, but contents himself with a diagram of the connections used by Lummer and Kurlbaum, and by giving an elementary demonstration of the electrical formulæ involved in its use.

It is a little singular that Callender's work with the platinum resistance thermometer should not be mentioned, and that an account of Boy's radiomicrometer should not be thought worthy of a place with the bolometer.

The author's treatment of this subject may be used as an illustration of a tendency often manifested in his work, which is a fair matter for criticism. From the student's point of view it is very desirable that every subject should in some place receive a fairly complete and consecutive treatment, to which reference may be made when desirable. The interdependence of the subdivisions of physics often makes this rule a difficult one to follow, but violations should be avoided when possible. The reader is frequently tempted to believe that Wüllner sins unnecessarily in this respect. In the case just referred to, we find important matter relating to the construction and calibration of thermo-electric elements for temperature measurements in at least four places in the second volume, with a reference to the one which is to follow for further information. The student has constant occasion to thank the author for a good index.

The chapter on the Mechanical Theory of Heat has not been materially changed from the form presented in the fourth edition. The author gives a good account of research on the subject, including the work of Rowland, and follows with a discussion of the first and second laws of thermodynamics, using to a great extent the notation and methods of Clausius, Zeuner, and Verdet.

The fifth chapter, which is the longest in the volume, presents an account of classical and recent experimental work upon the phenomena which accompany freezing, melting, and evaporation, and applies the results obtained to a discussion of the equations of condition proposed by Van der Waals, Clausius, and others.

Wüllner's manual as revised deserves to be ranked among the half-dozen text-books of physics which treat the subject in a fairly complete and

connected manner. Each one of these treatises probably has some distinguishing characteristic, by virtue of which it may claim a place in the working library of the student of physics; but it is always the case that special emphasis laid on one feature will inevitably call attention to any insufficiency in the treatment of other subjects.

Mention has already been made of certain features of Wüllner's work which recommend it to the student's use. It must be confessed, however, that the very fullness and detail referred to sometimes becomes a fault, but we can pardon this error more easily than the opposite one.

If our author does not push his mathematical discussion of theory as far as some, if we find he has omitted much interesting matter which lies on the borderland between physics and chemistry, we must remember that it is the experimental side of the subject which he has undertaken to present, and that he expressly disclaims any intention of treating the work in chemical physics with any degree of thoroughness.

One feature of Wüllner's treatment of his subject should commend his work to teachers: he constantly emphasizes, by the methods he employs, the important fact that it is unsafe teaching in physics which does not make the study of phenomena and the conditions which determine their manifestation the principal work of the student.

A. S. KIMBALL.

WORCESTER POLYTECHNIC INSTITUTE.

Electrical Measurements: a Laboratory Manual. By HENRY S. CARHART and GEORGE W. PATTERSEN. 8vo. pp. xiii + 344. Boston, Allyn & Bacon, 1895.

This book provides a "graded series of experiments for the use of classes in electrical measurements," "selected with the object of illustrating the general methods of measurement rather than applications to specific departments of technical work"; and it will for some purposes form a valuable addition to the growing list of laboratory manuals.

After an introductory discussion of units, measurements of resistance, current, electromotive force, quantity and capacity, self and mutual induction, and magnetism are treated in separate chapters, the chapters themselves, and the experiments in each, being arranged in the order of the difficulty which they present to the student. In all, recent forms of the appropriate instruments of precision are figured, and in most cases, described and discussed in greater or less detail. "Antiquated apparatus" is excluded, with such rigor that the authors apologize for describing even the tangent galvanometer, doing so, however, "because of its historical importance, if for no other reason." Lord Kelvin's quadrant electrometer is dropped without apology.

In general, the discussion of the methods of measurement consists of a description of the method, a deduction of the formula for calculating the quantity to be determined from the data of observation, and a numerical example. In some cases, the description is prefaced by a statement of the general idea of the method; but in many, the reader does not see what he is doing until he has read the account of how it is to be done. Best values of direct measurements and best arrangements of apparatus for the attainment of accuracy are determined in some cases, but not generally. Thus, although the fundamental property of the Wheatstone bridge is proved, no investigation is given as to the best resistance of galvanometer, or the best arrangement of battery and galvanometer. The reader is told with regard to the latter that Maxwell says such and such an arrangement should be adopted; but if he wishes to know for what purpose, or how Maxwell knew, he must go to Maxwell himself. But little information is given as to the degree of accuracy attainable with the different instruments and methods, sources of errors and methods of eliminating them, or other practiced details. The authors have evidently not intended to make the work self contained; and they give references to other manuals and to original papers, which are probably intended to atone for the omissions referred to. These references, however, are not sufficiently numerous for this purpose.

The introductory matter suffers from the effort after condensation. For example: "One kind of quantity may always be expressed in terms of two or three other kinds" (p. 1). "From Kupffer's observations Miller deduces the absolute density of water as 1.000013" (p. 6). "In the C.G.S. system the constant in the expression for f [the force between two magnetic poles] becomes unity" (p. 9). "There is no obvious relation between the two" [the electrostatic and electromagnetic systems of units] (p. 11). There should be a reference here to Rücker's paper on suppressed dimensions, *Philosophical Magazine* (Vol. 27, p. 104). "The numerical value of the E.M.F. between two points of a circuit, when there is no source of E.M.F. on this part of the circuit, equals the difference of potential between the same points" (p. 14). (The student should be referred to Nichol's *Laboratory Manual* (Vol. I., p. 182), for an admirable statement of the proper usage of the term "electromotive force.") "Every conductor of electricity offers greater or less obstruction to its passage. The researches of Dewar and Fleming on the resistance of metals at the temperature of boiling oxygen go to show that the resistance of all pure metals is zero at $-274°$ C., or the 'absolute zero.' The resistance of pure metals is, therefore, very nearly proportional to the absolute temperature" (p. 14). The deduction (p. 20) of the laws of resistance (its variation with length and cross-section of conductor) from Ohm's law is not made from this law, as formally stated

on p. 15, but from the law which properly bears the name of Ohm, and it involves other assumptions as well. Such slipshod expressions and reasonings, however, are confined to the introductory sections of the book, and are probably due to the desire to put much information into little space.

The book contains a very large selection of methods, and a selection which is not only large, but judicious, no important modes of measurement which are susceptible of accuracy having, so far as I have noticed, been omitted. With more references to original sources, it would thus form a valuable compendium for suggesting methods to the young investigator.

The chapters on the measurement of resistance and current occupy half the space, the former being especially full. Its weak point is the section on electrolytic resistance, in which the old form of Kohlrausch's method, with the electrodynamometer as indicated, is described, and no mention is made of the fact that for many years Kohlrausch has used the telephone as indicated. How great an improvement this is, in one respect, is shown by Wien in the last number of Wiedemann's *Annalen* (Vol. 58, p. 37). It is curious that with regard to this method the student is referred to a paper by Daniell, but not Kohlrausch himself. The chapter on electromotive force contains a detailed statement of the mode of constructing standard cells, which, being based on the wide experience of the senior author, is of great value. Methods involving the use of such cells are extensively introduced both in this and in other chapters. The discussion of quantity and capacity, induction and magnetism, occupy less space than the chapters which precede, but are equally full and are more exhaustive, so far as the number of methods referred to is concerned, than is usual in laboratory manuals.

Though the book assumes some knowledge of the calculus, the greater part of it is intelligible without such knowledge. In some cases in which the calculus is used it might, for the benefit of the non-mathematical reader, have been dispensed with without loss save of elegance. In one case in which it has been dispensed with — the discussion of the logarithmic decrement — the cogency of the reasoning suffers. The example appended to this discussion shows that such examples are not always worked out so as to give the most accurate result, the student being probably supposed not to aim at so high a degree of accuracy as to make this desirable.

The book is well gotten up, the type being good, the typography accurate, and the illustrations and diagrams excellent. It is provided, as all such books should be, with a full index, which very much facilitates reference.

J. G. MacGregor.

Lehrbuch der Electrochemie. By LE BLANC. 8vo. pp. 226. Leipzig, Oskar Leiner, 1896.

A careful and earnest study of the contents of this volume would certainly acquaint the student with the present standpoint of the subject of electrochemistry. The mathematics introduced are very simple. Only such simple differentials as $\frac{dE}{dT}$, expressing the rate of change of electromotive force with the absolute temperature, appear. The style of the author is very clear, and the subject-matter very systematically arranged. The book is primarily written for students beginning the study of theoretical electrochemistry. The reviewer has been able to make use of much of the contents to give technical students a thorough idea of the modern view of battery processes.

In the first chapter, the hypotheses of Grotthus, Clausius, and Arrhenius upon electrolytic conduction are discussed. The Grotthus hypothesis is shown to be contrary to the second law of thermodynamics. The kinetic theory of Clausius must be abandoned, also, since by this theory the "equivalent" conductivity should not increase with the dilution, as demanded by the Arrhenius dissociation theory. Chapter II. treats of the theory of Arrhenius; Chapter III. discusses the independent wandering of the ions; and Chapter IV. brings to our notice the conductivity of electrolytes. The phenomena noted in these chapters are linked together upon the theory of Arrhenius. The author points out that the van't Hoff law was instrumental in bringing Arrhenius to a comparison of the lowering of the freezing points of electrolytes and the electrical conductivity of the same. Upon these Arrhenius founded the theory of electrolytic dissociation.

The chapter upon electromotive force takes up nearly half of the book. Series are divided into the usual classes, reversible and non-reversible. A reversible process is carried through, and the analogy between osmotic and gas pressure pointed out. The expression used by Ostwald, "electrolytic solution pressure," is preferred to the name "solution tension" given it by Nernst. It would be almost an injustice to the book were one not to mention the neatness and simplicity with which the author points out that, just as the vapor pressure of water in contact with the liquid is the vapor pressure of saturation, so also the solution pressure of a substance or metal in contact with its solution is the osmotic pressure of saturation. Going out from this standpoint, series are treated after the Nernst method as machines working by osmotic pressure. Entropy is introduced in this connection as a "capacity factor" (not specific heat). This may afford an elementary, but scarcely a complete, idea of the phenomena of entropy.

In a reversible process applied to batteries the term entropy recurs in the later equation of von Helmholtz,

$$CE - Q = CT\frac{dE}{dT},$$

where C, E, Q, and T represent current, electromotive force, "heat-toning," and absolute temperature, respectively. The equation shows that the temperature coefficient of a series will be positive or negative, according as the chemical energy is less or greater than the electrical energy.

The galvanic series are treated in the following order. Concentration Series, embracing (1) various concentration of substances giving ions, (2) various ionic concentrations, and (3) concentration double series; Liquid Series, General Considerations upon Concentration — and Liquid Series, Thermo Series, and Chemical Series.

In the Concentration Double Series,

$$Zn \mid ZnCl_2(conc) \mid HgCl \mid Hg \mid HgCl \mid ZnCl_2(dilute) \mid Zn,$$

we have two cells of the same kind in opposition. It is maintained that this is not the same as

$$Zn \mid ZnCl_2(conc) \mid ZnCl_2(dilute) \mid Zn.$$

In the latter case when a current passes, besides zinc going into solution at one electrode and precipitating at the other, there is a wandering of the $\overset{+}{Zn}$ and $\overset{-}{Cl}$ ions from the concentrated to the dilute solution. In the calomel double series such a wandering is impossible. For this double series the electromotive force equals

$$\frac{3}{2}\frac{RT}{c}\log_e\frac{p}{p_1},^1$$

where p and p_1 are the osmotic pressures in the concentrated and dilute solutions respectively, and c is the number of coulombs, 96540, per gram equivalent. Now, in the second series, it can be easily shown that the electromotive force equals

$$\frac{u-v}{u+v}\frac{RT}{2c}\log_e\frac{p}{p_1},$$

where u and v are the wandering velocities of the kathion and anion respectively. The condition for equality is

$$\frac{u-v}{u+v} = 3.$$

[1] This equation is the author's, the following one the reviewer's. The latter is also a particular form of an equation of the author in Liquid Series.

If n denote the transference number of the kathion, then

$$n = \frac{u}{u+v}; \text{ and } 1 - n = \frac{v}{u+v}.$$

The solution of these equations gives:

$$n = 2; \; u = \tfrac{2}{3}; \text{ and } v = -\tfrac{1}{3}.$$

This means that two equivalents of the kathion, and one equivalent of the anion, pass into the dilute solution for every equivalent of current generated. One kathion is, however, given up at the electrode, which leaves a net gain, in the dilute solution, of one positive, and one negative, equivalent. Since one anion equivalent appears at the other electrode, the concentrated solution loses two equivalents of both ions, — one equivalent taking part in current conduction, and one equivalent passing to the dilute solution. The condition of affairs could not, indeed, be much simpler. Whether or not it is the actual condition could be found by testing the solutions after the passage of a definite current. The objection that the anion and kathion do not wander in such ratios can scarcely be raised, for one might also say, the two ions do not usually wander in the same direction. If diffusion and potential difference change the direction of an ion, why can they not modify its relative velocity?

The drop electrode method of measuring the electromotive force of each terminal is discussed, and special attention called to the Ostwald constant electrode

$$\text{Hg} \mid \text{HgCl in normal KCl} = -0.56 \text{ volts},$$

which may be combined with any other electrode and solution. From the electromotive force of the whole and that of the known mercury electrode, the unknown electromotive force of the other electrode is determined. The drop electrode method is thus obviated. The method should give good results if the known single potential be constant and reliably determined. Several observers obtain the same voltage for the electrode and certify to its constancy. Many persons will find the author's graphic treatment of this subject of interest.

The chapter on polarization is next in importance and interest. The subject matter and conclusions are largely drawn from the author's own investigations. The electromotive force of polarization of H and O between black platinum (platinirites platinum) electrodes is 1.07 volts; that between plain platinum electrodes is 1.70 volts. In the former case we have equilibrium between the gas absorbed by the electrode and the solution; in the latter case the electrolyte must contain much more gas at the electrode before it is in equilibrium with the outside pressure. The elec-

tromotive force of 1.70 volts could then be lowered by reducing the atmospheric pressure. This is found to be true. It is to be noted, too, that 1.70 volts is the electromotive force of acids and bases yielding hydrogen and oxygen, and this value is independent of the concentration. For acids whose polarization value is below 1.70 volts, the value tends toward 1.70 volts as a maximum on diluting the solution. On reaching this value, hydrogen and oxygen are given off.

Le Blanc's conclusion upon these phenomena is in sharp contrast to the widespread view of secondary action. For example, in a solution of sulphuric acid and water, he opines that all ions take part in the conduction in proportion to their respective concentration, but at the electrode only those ions are given up which are easiest given up,[1] *i.e.* those which have the lowest solution pressure, or lowest electromotive force of polarization. The ions are liberated which require the least expenditure of energy. How then can an electromotive force of polarization above 1.70 volts exist, *e.g.* that of zinc sulphate equal to 2.35 volts? The theory protects itself very cleverly. In this and similar cases, the evolution of hydrogen at the kathode would involve the production of hydroxyl ions, the maximum quantity of which are already present, and the electromotive force therefore rapidly rises to the evolution of another product.

Chapter VIII. is a short additional contribution of nine pages upon practical galvanic batteries and the lead accumulator. This is the first attempt that has been made to offer any explanation of the lead accumulator from the present standpoint of electrolytic processes. Devoting four and one-half pages to such a subject, one cannot give any complete theory of the lead cell, but the reviewer is inclined to think that this method of treatment can be so amplified as to explain much of the peculiar behavior of this cell. The author shows that the principal reaction of the cell upon discharge is

$$PbO_2 + 2\,H_2SO_4 + Pb = 2\,PbSO_4 + 2\,H_2O + 87{,}000 \text{ cal.}$$

The old theory also agrees to this reaction. Under the assumption of a zero temperature coefficient, this would give us an electromotive force of 1.885 volts. The electromotive force during discharge is for a considerable period of time not far from this value. Hence the small error in applying the Kelvin formula. However, the discharging electromotive force is often 2.1 volts. The author could have shown that under these circumstances the cell should have an appreciable temperature coefficient. An application of the von Helmholtz formula before mentioned shows that the cell would then cool during discharge, as noted by Dr. Duncan. The charging electromotive force goes still higher. The temperature coefficient would

[1] This view seems to have first been held by Hittorff.

therefore be still higher, and the heating would be greater than the cooling in the previous case. Professor Ayrton has shown that this heating amounts to seventeen per cent of the entire energy of the cell, even after allowance is made for the C^2R loss within the cell. The fall of potential during discharge can be easily explained upon the principle of "solution tension" and osmotic pressure. The author treats this too briefly entirely. The theory points out the necessity for a concentration electromotive force, opposing both the charging and discharging currents. The author has made no allusion to this action, which alone would make it impossible to obtain a high efficiency when large currents are taken from the cell.

It is to be regretted that there is no index to the book. The references to the original literature could have been increased to an advantage.

The author acknowledges his indebtedness to his personal contact with and writings of Professor Ostwald. The reviewer regrets very much that he has had the opportunity of making only a hasty inspection of the recent large and interesting volume of Professor Ostwald upon the same subject.

B. E. MOORE.

UNIVERSITY OF ILLINOIS,
June, 1896.

The Alternate Current Transformer. Vol. I. By J. A. FLEMING, F.R.S. 8vo, pp. 606. London, The Electrician Printing and Publishing Company, 1896.

In this new edition of a well-known work, the author has followed closely the lines of the earlier edition, but has amplified the treatment in places, and has eliminated some of the portions which have become antiquated. No book on the transformer is more replete with information than this work, and none are better qualified than Dr. Fleming to speak with authority on the subject. It is with disappointment, therefore, that the reader finds the same lack of continuity and disregard for sequence which characterized the earlier edition. The book contains too much patchwork for student use, and the facts contained are rather diffuse and scattered for the busy engineer.

F. B.

The Principles of the Transformer. By FREDERICK BEDELL, Ph.D. 8vo, pp. xii+416. Figs. 250. The Macmillan Company, 1896. (*Received.*)